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RESEARCH REPORT

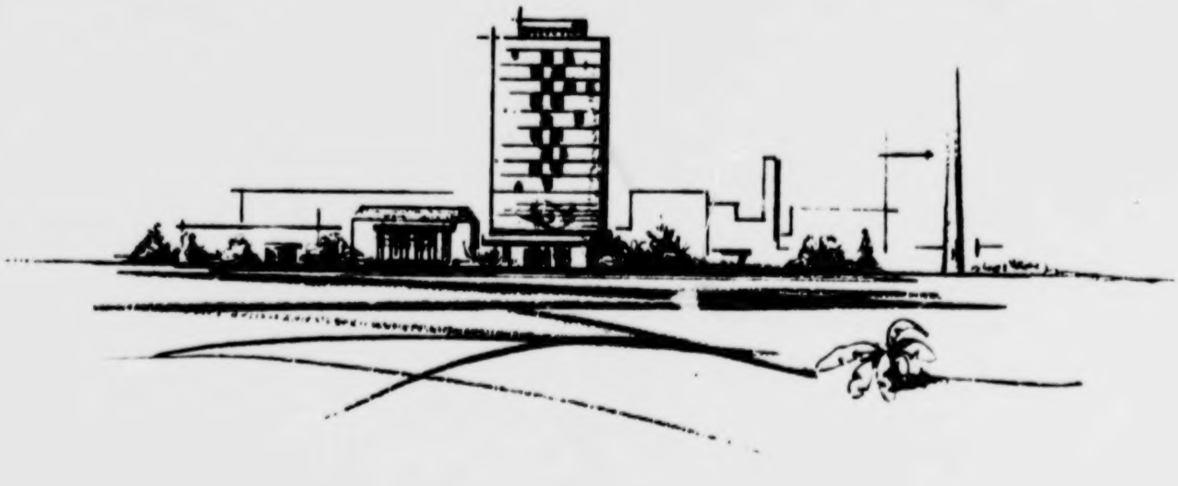
DESIGN OF AN OVERVIEW SYSTEM FOR
EVALUATING THE PUBLIC-HEALTH HAZARDS
OF CHEMICALS IN THE ENVIRONMENT

Volume I. Test-Case Studies

to

THE UNITED STATES
PUBLIC HEALTH SERVICE

July, 1967



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FINAL REPORT

on

DESIGN OF AN OVERVIEW SYSTEM FOR EVALUATING THE PUBLIC-HEALTH HAZARDS OF CHEMICALS IN THE ENVIRONMENT

Volume I. Test-Case Studies

to

THE UNITED STATES
PUBLIC HEALTH SERVICE

July, 1967

by

G. A. Lutz, S. B. Gross, J. B. Boatman, P. J. Moore,
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Prepared under Contract No. PH-86-66-165

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PREFACE TO VOLUME I

Volume I contains a review of the potential environmental health hazards due to utilization of mercury, nickel, vanadium, and fluorocarbon compounds, and of the chemicals used by the pulp and paper industry. Volume II describes recommendations for an Overview System based on the experiences gained from the information-analysis exercises described in Volume I.

TABLE OF CONTENTS

Page

INTRODUCTION 1

OBJECTIVES 1

APPROACH TO THE STUDY 2

Selection of Model Studies 2
Collection of the Information 3
Evaluation and Interpretation 3

SECTION 1. ENVIRONMENTAL HAZARDS OF MERCURY 4

Occurrence, Production, and Consumption 4
Use Pattern. 4
Mercury Toxicity 5
Environmental Mercury 5
Recommendations. 6

SECTION 2. ENVIRONMENTAL HAZARDS OF VANADIUM 8

Occurrence, Production, and Consumption 8
Use Pattern. 8
Vanadium Toxicity 8
Environmental Vanadium 9
Recommendations 9

SECTION 3. ENVIRONMENTAL HAZARDS OF NICKEL 11

Occurrence, Production, and Consumption 11
Use Pattern. 11
Nickel Toxicity 12
Environmental Nickel 12
Recommendations 12

SECTION 4. ENVIRONMENTAL HAZARDS OF FLUOROCARBONS 14

Production and Consumption 14
Use Pattern. 14
Fluorocarbon Toxicity 14
Environmental Fluorocarbons 15
Recommendations 15

SECTION 5. ENVIRONMENTAL HAZARDS OF PULP AND PAPER CHEMICALS . 17

Production and Consumption of Paper Products 17
Use Pattern 17
Pulp and Paper Chemicals Toxicity 17
Environmental Inputs From Pulp and Paper Chemicals . . 18
Recommendations 18

TABLE OF CONTENTS
(Continued)

Page

APPENDIX A

MERCURY A-1

- Economics Information A-1
  - Natural Occurrence A-1
  - Domestic Production and Reclamation A-1
    - Primary Sources A-1
    - Secondary Sources A-3
    - Refining A-4
  - Use Pattern. A-6
    - Mercury-Cell Chlorine Production A-7
    - Apparatus, Instruments, and Related Uses A-8
    - Paint A-10
      - Antifouling Agents. A-10
      - Mildewproofing Agents A-10
    - Agriculture A-11
    - Pharmaceuticals A-12
    - Dental Preparations A-19
    - Catalysts. A-19
    - Amalgamation A-22
    - Paper and Pulp Manufacture A-22
  - Recent Research A-23
- Toxicity Information A-24
  - Incidence of Mercury Poisoning A-24
  - Pharmacology A-26
    - Determination of Mercury A-26
    - Mechanism of Action. A-26
    - Absorption, Distribution, and Excretion A-26
    - Mercury in Tissues A-27
  - Toxicology A-28
    - Clinical Mercury Poisoning A-28
    - Acute Mercury Poisoning A-29
    - Chronic Mercury Poisoning A-29
    - Hypersensitivity A-30
    - Diagnosis of Mercury Poisoning A-30
    - Therapy for Mercury Poisoning A-30
  - Lethal Dosages of Mercury. A-31
  - Tolerance to Mercury A-31
    - Limits for Mercury in Industrial Air A-32
    - Limits in Water A-32
    - Limits in Foods A-32
    - Limits in Drugs A-32
- Environmental Hazards A-33

TABLE OF CONTENTS
(Continued)

Page

REFERENCES A-34

- Economics Information A-34
- Toxicity Information A-36

APPENDIX B

VANADIUM B-1

- Economics Information B-1
  - Natural Occurrence B-1
  - Domestic Production B-2
  - Recovery Methods B-5
  - Use Pattern B-6
    - Steel B-7
    - Castings B-9
    - Nonferrous alloys B-9
    - Electrochemical Systems B-9
    - Catalysts and Chemicals B-9
    - Glass and Ceramics B-14
    - Wear-Resistant Facings B-14
    - Magnets B-14
  - Recent Research B-14
- Toxicity Information B-15
  - Incidence of Vanadium Poisoning B-15
  - Pharmacology B-16
    - Mechanism of Action B-16
    - Absorption, Distribution, and Excretion B-16
    - Toxic Dosages in Animals and Man B-17
    - Symptoms of Vanadium Poisoning B-17
    - Diagnosis and Treatment B-17
    - Tolerance Limits B-18
- Environmental Hazards B-18

REFERENCES B-18

- Economics Information B-18
- Toxicity Information B-19

APPENDIX C

NICKEL C-1

- Economics Information C-1
  - Natural Occurrence C-1
  - Production C-1
    - Primary Sources C-1
    - Secondary Sources C-3

TABLE OF CONTENTS
(Continued)

Page

- Recovery Methods . . . C-3
- Use Pattern . . . C-4
  - Alloys . . . C-8
  - Electroplating . . . C-11
    - Anodes . . . C-11
    - Electrolytic Chemicals . . . C-11
  - Catalysts . . . C-13
  - Magnets . . . C-17
  - Ceramics . . . C-17
  - Other Uses . . . C-18
- Recent Research . . . C-21

Toxicity Information . . . C-22

- Incidence of Nickel Poisoning . . . C-22
- Pharmacology . . . C-23
  - Mechanism of Action . . . C-23
  - Absorption, Distribution and Excretion . . . C-24
- Toxicology . . . C-24
  - Acute Poisoning . . . C-24
  - Nickel Sensitization . . . C-25
  - Carcinogenic Effect . . . C-25

Environmental Hazards . . . C-25

REFERENCES . . . C-26

- Economics Information . . . C-26
- Toxicity Information . . . C-28

APPENDIX D

FLUOROCARBONS . . . D-1

Economics Information . . . D-1

- Production . . . D-1
  - Fluorochemical Plants . . . D-1
  - Methods of Preparation . . . D-2
  - Manufacturers and Distributors . . . D-4
- Use Pattern . . . D-6
  - Nonplastics . . . D-6
  - Plastics . . . D-8
- Recent Research in Fluorochemicals . . . D-9

Toxicity Information . . . D-10

- Monomeric Aerosols, Refrigerants, and Anesthetics . . . D-12
- Plastic Fluorocarbons . . . D-12

Environmental Hazards . . . D-13

REFERENCES . . . D-14

- Economics Information . . . D-14
- Toxicity Information . . . D-15

TABLE OF CONTENTS
(Continued)

APPENDIX E

PULP AND PAPER CHEMICALS . . . .

- Economics Information . . . .
  - Location and Capacity of Pulp and Paper Mills . . . .
  - Domestic Production of Pulp and Paper Products . . . .
  - Use Pattern . . . .
    - Pulp Processing . . . .
    - Neutral Sulfite – Semichemical Pulping Process . . . .
    - Pulp Bleaching . . . .
    - Paper and Paperboard Manufacture . . . .
  - Recent Research . . . . E
- Toxicity Information . . . . E
  - Toxicology . . . . E
  - Chemical Contaminants Resulting From Pulp and Paper Manufacture . . . . E
    - Pulp Processing . . . . E
    - Bleaching . . . . E
    - Paper and Paperboard Manufacture . . . . E

REFERENCES . . . . E

- Economics Information . . . . E
- Toxicity Information . . . . E

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INTRODUCTION

The National Environmental Health Sciences Center has the general mission within the Public Health Service of identifying and evaluating the present and potential hazards to public health of environmental contaminants. Evaluation of hazards has many aspects. Hazardous materials must be identified, their sources described, trends toward increasing or decreasing levels of human exposure estimated, and possible detrimental effects on health recognized currently or anticipated and obviated by preventive measures. To meet this responsibility, an active and continuing program to appraise the nature, significance, and possibilities for control of chemical contaminants is being instituted.

This report is an initial effort in the development of a program that will allow the Public Health Service to maintain an active overview of chemical contaminants that are now, or are likely to be, present in the environment. The objectives are defined, and the recommended approach to their realization is discussed in the following sections. To illustrate the methods of applying the approach, as well as to develop the base for considering eventually all possible hazards, five specific contaminant classes are selected for individual treatment in separate sections following the general discussions. These sections summarize the contamination potentials of mercury, vanadium, nickel, fluorocarbons, and pulp and paper production, respectively. Conclusions and recommendations for each contaminant are offered at the end of each summary. Finally, five Appendixes contain background details and literature sources for each contaminant class.

OBJECTIVES

The specific objectives of this effort were similar to most informational studies of complex technical subjects. This study seeks to do the following operations in sequence:

(1) To define the areas in which the study is to be concentrated so that reasonably complete treatment and useful results can be presented within within the limits of available time and funds

(2) To identify sources of information and to collect comprehensive source data

(3) To select from collected sources the pertinent and significant subject matter for summarization and inclusion in the study report

(4) To appraise and interpret the selected subject matter in terms of the defined mission of the National Environmental Health Sciences Center

(5) To recommend or suggest actions and their priorities that might be taken, subject to policy decisions by the Center's staff

(6) To develop and illustrate by example in this report the experience that will permit efficient and effective interpretation of new data whenever objectives are expanded, new classes of hazards are recognized or selected, selected classes are reviewed, or the mission effort is redefined or redirected.

This study was intended to assist in setting up an overview system for chemical contaminants, with pertinent information assembled in a form that can be referred to quickly as a basis for sound decisions on what activities should be undertaken on a priority basis. As far as possible, the necessity for research to fill gaps in existing knowledge is indicated. At times, preferences may be suggested for in-house studies at facilities of the Center, for contract research sponsored by the Center, or for grants or other procedures to encourage long-range studies of background factors that influence contamination levels.

APPROACH TO THE STUDY

Selection of Model Studies

The five model studies of specific contaminants were selected because they represent different chemical and toxicological profiles considered essential to establish parameters for an overview system:

(1) Mercury has been used in many different applications for a long time. Its contamination cycle is presumably widely distributed. Acute mercury poisoning in man was recognized and studied early in the development of human toxicology.

(2) Vanadium applications are growing; the usage pattern is diverse and differs from that of mercury. Vanadium compounds are generally regarded as toxic, so that trace exposures may be critical at a level lower than is generally recognized.

(3) Nickel usage is growing in many different applications of metallurgy, chemistry, and technology. Use of nickel in stainless steel alloys provides widespread contact with man. However, the potential for toxic reactions is generally believed to be low.

(4) Fluorocarbons are finding many use patterns, some of which involve multiple and widespread exposures in domestic usage. The phenomenal growth in usage makes these compounds new enviromental burdens.

(5) Pulp and paper chemicals are used in large volume and continue to change and increase in usage, so that harmful contact with man must be safeguarded.

Collection of the Information

In these pilot studies, pertinent information was identified and selected by examination of appropriate subject indexes of journals, abstracts, and current periodicals. Screening was done in this instance by the two professional scientists who were to make the evaluation and interpretation of the subject matter. One searched primarily the subjects dealing with the contamination cycles in the environment, and the other those concerned with physiology and toxicology of the contaminants in their effects on man and animals. This procedure served not only to collect information, but also to identify key subjects and sources that might be suggested for use by technical specialists in collecting and screening background data for final interpretation by others in a continuing overlook program.

Evaluation and Interpretation

The combined activities of collection and evaluation were directed specifically toward the following interpretations:

(1) Current status of environmental contamination by each of the five selected types of contaminants. This involves examination of the complete cycle of the contaminants from their primary source, through usage patterns, losses, and final application or disposal. Within this cycle, the points or areas of contact with man are noted.

(2) Current status of environment-related medical knowledge of the effects of each type of contaminant. This includes both toxicologic and epidemiologic information.

(3) Technological changes that appear likely to lead to the entrance of new contaminants of the selected types, or to significant changes in contamination by the contaminants studied.

(4) Demographic-related changes that would affect the degree of population exposure to these types.

(5) Deficiencies in the available information in these categories, and the type and location of research facilities and capabilities that might be used to develop the required information.

SECTION I. ENVIRONMENTAL HAZARDS OF MERCURY

Occurrence, Production, and Consumption

Mercury usually occurs as the red cinnabar ore, mercuric sulfide. Important deposits are found in Europe, South America, Asia, and North America, especially the western part of the United States. It is estimated that the outer layer of the earth's crust contains 2.7×10^{-6} percent mercury and that the oceans contain 50 million metric tons.

Assuming 10 percent losses of mercury from mining and refining operations during 1965, about 170,000 lb of mercury entered the environment as refractory slag, volatiles during refining, and wastes collected during smelting. During the same period, assuming 5 percent loss during secondary production, an additional 175,000 lb of mercury entered the environment from secondary sources.

During the 20th century, mercury consumption in the United States has totalled about 163,000,000 pounds. In terms of present population, this figure averages about 0.8 pound per capita. During the last decade, annual consumption has risen from an average of 4,000,000 pounds during the period 1956 to 1960, to an estimated 6,000,000 pounds in 1966.

The above figures suggest that we must expect a certain background level of mercury practically everywhere. It must also be assumed that a general mercury cycle occurs in nature. To understand this cycle, we need to be aware of the amounts of mercury that occur in air, soil, water, and living organisms as well as the biological and chemical-physical transfer mechanisms.

Use Pattern

An examination of the use pattern for 1965 indicates how mercury is added to the environment. Although there have been fluctuations in quantities in the use categories reported, generally there have not been any changes in the categories themselves during the last decade. The electrolytic preparation of chlorine and caustic soda has required and will continue to require large quantities of mercury. It is estimated that by 1970, about 16,000 flasks* will be consumed annually in the electrolytic production of chlorine. This amounts to about 44 flasks (3,300 lb) per day. This could be a source of contamination for water and for air. Agriculture, including the use of fungicides, herbicides, and insecticides, adds about 250,000 lb of mercury to soil, water, and the air. About 575,000 lb of phenyl mercurials, mildew-proofing materials for paints, found their way into the air, streams, and the soil. Antifouling agents in paints accounted for about 20,000 lb of mercury in the air, streams, and soil. Through the use of phenyl mercurials by the paper industry about 45,000 lb per year of mercury were added to the waters. Through the burning of paper, some of this entered the atmosphere. The use of approximately 250,000 lb of mercury in pharmaceuticals, especially as diuretics and anti-infectives led to direct contamination of man with mercury and subsequent addition to waters and the atmosphere. The preparation of catalysts required approximately 75,000 lb of mercury that found their way into air, water, and probably soil. Likewise, amalgamation led to about 37,000 lb of mercury for release to soils and waters. About 125,000 lb of mercury were used in dental preparations. Some of this probably became an environmental hazard.

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*A flask = 76 lb.

Mercury Toxicity

All mercury compounds, when present in the body in sufficient quantity, are toxic. The amount present depends on the relative rates of uptake and removal from the body. These rates vary with the type of compound. Elemental mercury and many of the organic compounds can be ingested with little ill effect. However, all inhaled and injected mercurials are absorbed rapidly. Organic mercurials tend to accumulate in lipoid tissues, while the inorganic compounds are absorbed mainly by the kidney. Absorbed mercury is usually excreted in the urine, and in some patients can be detected in the breath.

An awareness of the presence of mercury, as may be the case in industrial operations, is necessary to prevent toxic effects. Usually, the diagnosis of acute mercury poisoning is easily made because of the availability of a suitable history of mercury exposure. It is often difficult to diagnose chronic mercury poisoning because one or more of the classical symptoms of gingivitis, tremor, and mental deterioration may be absent, with only vague symptomatology evident. "Normal" blood and urine mercury levels are less than 0.5μg/100 ml and less than 100 μg/24 hours, respectively. Blood and urine analyses for mercury are not well correlated with symptoms of poisoning. It is possible for individuals to have higher levels of body (blood, urine, and/or tissue) mercury. In many such cases, the source of the mercury will not readily be apparent.

If acute poisoning is not immediately lethal, treatment with complexing agents and other supportive methods are effective. Damage caused by chronic poisoning frequently is intractable. The body can endure a certain amount of mercury without any apparent harm. The amount tolerated by individuals varies. In addition, estimates of allowable body concentrations vary considerably.

Safe concentrations of airborne mercury are set in this country at 0.1 mg/m^3 of inorganic Hg and 0.01 mg/m^3 for organic mercurials. In Russia, these levels are set at 0.003 mg/m^3.

Environmental Mercury

Mercury in the open environment has not been monitored quantitatively or in detail, but differences in distribution, solubility, and volatility of organic and inorganic mercurials must result in a complex ecology of mercury throughout nature.

A variety of qualitative reports support this conclusion. Mercury from industrial smoke stacks has been reported to kill plants on nearby fields. Air containing mercury in the home has been reported to result in morbidity and mortality. However, in a study involving a mercurial paint, the hazard was short-lived and probably tolerable to those individuals not previously exposed to mercury. Unavailable, but badly needed, is information on volatiles that may be released from mercurial-containing plastics and paints. Sources of mercury from solid-waste landfills for mercury-containing residues constitute a potential atmospheric and water contaminant. Man and animals exposed to large quantities of mercury may exude dangerous quantities of mercury to the surrounding environment.

Because of the use of mercurial pesticides, accumulation of mercury in food products can be anticipated. Numerous reports appear in the literature describing the use of such agents to control food pests. Standards have been established for the upper limits of pesticide mercury residues that can be safely accepted in plants. The use of mercurials in paper products for the wrapping or storage of food is prohibited.

Mercury has been found in the food fish taken from Minamata Bay in Japan, into which industrial wastes containing mercury are discharged. In Sweden, mercury has been found in birds and fish. These observations indicate that mercury from environmental sources can accumulate in the food chain and be transferred to man.

Few cases of actual mercury intoxication have been reported from the major uses of pharmaceutical mercury compounds as diuretics and anti-infectives (antiseptics). With the advent of the thiazides as diuretics, the use of mercurials in this field will dwindle. However, present usage suggests that human waste from personnel treated with mercurial diuretics could contribute to water and soil contamination. The use of mercurials as anti-infectives could lead to undesirable skin absorption of these drugs and the subsequent return of the mercury to the environment.

The potential danger of mercury in drinking water has been recognized. In this country, no standards for permissible mercury content of water have been recommended, partly because the total picture of the effects of man's exposure to mercury needs to be clarified. Simple filtration and chlorination techniques for water probably are insufficient to remove soluble mercury. Ion exchange may be required to control undesirable concentrations of content in drinking water, streams, and rivers, if these are found to exist.

Some organic mercurials are readily absorbed percutaneously, which may occur during manufacture or application of mercurials. For example, the worker in industrial plants may be inadequately protected from take-up of mercury through the skin. Also, percutaneous absorption of pesticides by farmers has been noted. However, absorption of mercurial fungicides from swimming pool paints has to our knowledge not been reported.

Thus, the assembled evidence points to a variety of sources and exposures to mercury in man's environment; it is possible that some of the exposure potentials remain unrecognized.

Recommendations

From our review of mercury as an environmental chemical contaminant, it is obvious that a considerable amount of mercury has been cycled through our environment. We know that mercury can be toxic in acute and chronic levels. We do not know what chronic low-level exposure damage is possible. At present, potential mercury toxicity seems to be confined mainly to the industrial environment, and this is generally well controlled, at least in this country. We have little or no information as to where the mercury that is being cycled through our environment is going. Therefore, the following recommendations are made:

(1) We need to establish base levels of mercury in our air, water, and food. This can be relatively readily accomplished by analyzing samples from

our National Air Sampling Network, our National Water Quality Network, and the FDA's food-policing system. This should enable us to establish the amount of exposure to mercury to which our population might be exposed.

(2) Based on these levels, research should be carried out on the chronic effects of mercury in animals.

(3) Epidemiological case studies should be carried out by reviewing the available case reports for patterns indicative of mercury poisoning. Sampling investigations in populations most probably exposed to higher levels of mercury should be made.

(4) Human autopsy specimens from across the country initially, and subsequently from those areas that show substantial mercury content should be analyzed for base-line body-load studies. Periodic samplings should be taken to detect possible increases in body load.

(5) Economic surveillance of mercury utilization needs to be evaluated routinely, carrying on from the bases initiated in this study. Mercury contamination in chlorine production is especially important. Mercury in the broad categories of instrumentation, redistillation, and reclamation, is a likely source of environmental contamination and therefore, should be subjected to continuous surveillance.

SECTION 2. ENVIRONMENTAL HAZARDS OF VANADIUM

Occurrence, Production, and Consumption

Vanadium occurs in ores found in Africa, South America, and North America. Carnotite, a uranium-vanadium ore, is especially abundant in western Colorado and eastern Utah. It serves as a strategic source of vanadium. The ashes of bitumens, asphalts, and coals may yield up to 12 percent vanadium. It is estimated that trace concentrations in the oceans aggregate about 7,500 million metric tons of vanadium. Estimated recoverable reserves of vanadium ores in the United States total about 600,000 tons of contained vanadium metal — about triple the projected 40-year demand.

Roasting, leaching, precipitation, and oxidation are used in the preparation of vanadium pentoxide from ores; reduction of the pentoxide in the presence of iron oxide and fluxes leads to ferrovanadium. Reduction of vanadium pentoxide, ferrovanadium, vanadium dichloride, or vanadic acid in the presence of calcium or calcium and iodine gives pure vanadium.

During the 10-year period 1956 through 1965, vanadium consumption in the United States totalled about 25,000 tons. In terms of present population, this represents about 0.25 pound per capita. Consumption has risen from an annual average of 2,000 tons during the period 1956 to 1960 to 5,660 tons in 1966.

Use Pattern

Of the estimated 5,660 tons of vanadium produced in 1966, 84 percent, or 4,754 tons, was used in the steel industry as a constituent of high-strength, low-alloy steels and 11 percent, or 622 tons, in nonferrous alloys, especially titanium and aluminum alloys. Most of the remaining 5 percent (284 tons) went into various chemical, electrochemical, catalytic, and ceramic applications. Major catalytic uses for vanadium are in the manufacture of sulfuric acid, the oxidation of numerous organic compounds to commercial products, and the polymerization of olefins to synthetic rubbers. A primary battery containing a zinc anode and a vanadium pentoxide cathode has been developed. Compounds of vanadium, such as vanadium pentoxide and vanadium trioxide, are used in the ceramic industry for glazes and enamels. Vanadium boride, vanadium carbide, vanadium nitride, and vanadium silicide are used in the tool and die industry for applications in which hardness is required.

Vanadium Toxicity

Vanadium toxicity has not been studied extensively, nor has it provided the variety of hazards experienced from mercury, as discussed previously. The relatively few cases of vanadium toxicity reported in the literature are confined mainly to industry — for example, the inhalation of dust and fumes during mining and refining operations. Under these conditions, the chief impact appears to be on the lungs, kidneys, and intestinal tract. Various enzyme systems have been shown to be affected by vanadium compounds. Some of the compounds reduce blood cholesterol levels and reduce cholesterol and phospholipid metabolism in the liver. Vanadium also inhibits the sulfhydryl-dependent succinic dehydrogenase of liver and reduces the levels of cystine in hair and fingernails.

Studies on the absorption, distribution, and excretion of vanadium compounds have been reported. Injected compounds are more readily absorbed and distributed than inhaled compounds. Since vanadium is absorbed only moderately well from the gastrointestinal tract, ingestable forms usually are nontoxic. Oral, injected, or inhaled vanadium is excreted largely by the kidney. Retention of administered vanadium compounds is greatest in the liver and kidney, although significant quantities are retained by the skeleton. Levels of vanadium in the tissues of men who have not been exposed to vanadium are usually less than 1 microgram per gram of ashed material.

Acute human symptopathology is usually associated with inhalation of dust, which produces irritant reactions of the eyes, nose, throat, and upper respiratory tract. These symptoms can progress to nasal catarrh, nose bleeding, bronchitis, pneumonia, nausea, vomiting, and abdominal pains. Greenish tongue is common among vanadium workers, but is of no known toxicological significance. The lethal dosage to man is approximately 30 mg of vanadium pentoxide per 70 kg of body weight.

Diagnosis of vanadium toxicity is based on evaluation of contraindications and on urine assay. Treatment consists mainly of protecting the individual from further exposure. In this respect, threshold limits of 0.5 mg of vanadium pentoxide dust/m^3 and 0.1 mg/m^3 for fumes have been established.

Environmental Vanadium

The handling and use of vanadium ores and compounds in industrial operations is the major potential source of vanadium in significant amounts in the environment. Exposures to (1) dust in mining, and processing operations, (2) dust developed in the cleaning of oil-fired burners or gas turbines (because vanadium is present in all fuel oils, and it concentrates in distillation and combustion residues), (3) dust (pentoxide) in glazing and enameling operations, and (4) readily volatile vanadium halides that are used in the manufacture of synthetic rubber, all constitute potential environmental hazards of vanadium. Although the use of vanadium in a broad range of catalytic reactions does not suggest a serious environmental hazard, the use of vanadium compounds under any conditions where they might contaminate the atmosphere, come into direct contact with personnel, or be dumped as waste, should be considered as potentially harmful to the health of man.

Recommendations

From our review of the usage pattern, it appears that increasing quantities of vanadium may be entering the environment. We also know that vanadium can be toxic in acute and chronic levels. However, we do not know the effect on our populace of vanadium in air and water, as measured by the National Air Sampling Network and the National Water Quality Network. Therefore, the following recommendations are made:

(1) Maintain monitoring of air and water, and initiate research to determine chronic effects in animals of vanadium concentrations encountered in air and water.

(2) Monitor new mining, smelting, and refining operations to determine what effect possible sudden environmental enrichment of vanadium may have on the population.

(3) Establish body-load values through autopsy, particularly in areas where monitoring indicates substantial vanadium in the environment.

(4) Because of the volatility of the halides of vanadium, monitor new and established use patterns of these compounds for vanadium levels.

SECTION 3. ENVIRONMENTAL HAZARDS OF NICKEL

Occurrence, Production, and Consumption

The two commercially important nickel minerals are pentlandite, found in Ontario, and garnierite, found principally in New Caledonia. Nickel comprises about 0.01 percent of igneous rocks. It is present in trace amounts in marine organisms. It has been estimated that there are 2,500 metric tons of nickel in the oceans.

About 13,000 tons of nickel were mined in the United States in 1965. In addition, nickel salts containing approximately 4,300 tons of nickel were produced as by-products of copper refining and chemical manufacture. Assuming a 90 percent recovery, about 1,730 tons of nickel were returned to the environment from these two sources of production.

During the period 1956 through 1965, nickel consumption (exclusive of scrap) has totalled about 1,230,000 tons. Nickel-scrap consumption during the same period was about 200,000 tons. Present consumption for the two categories is about 0.06 ton per capita. During the last decade, annual consumption (including scrap) has risen from an annual average of 125,000 tons during the period 1956 to 1960 to an estimated 195,000 tons during 1965.

The above figures suggest that a certain background level of nickel may constitute an environmental hazard. It must be assumed that a general nickel cycle occurs in nature. To understand this cycle, we need to be aware of nickel that occurs in air, soil, water, as well as the biological and chemical-physical transfer mechanisms.

Use Pattern

An examination of the use pattern for 1965 indicates how nickel is added to the environment. With the exception of a slight decrease in ceramics, nickel consumption in the United States during the last decade increased in all categories, i.e., ferrous alloys, nonferrous alloys, high-temperature and electrical resistance alloys, electroplating, catalysts, magnets, and other products. Comparatively large gains were achieved in ferrous stainless steels, nonferrous alloys and in the "other" category, which includes chemical uses. Because of their excellent corrosion resistance, nickel and high-nickel alloys are used in many food-processing operations. This could be a source of contamination for man, water, and soil. It is estimated that about 25,000 tons of nickel were consumed during 1965 in electroplating and in the manufacture of electrochemicals. Both these sources could serve as points of contamination for water and soil.

Nickel carbonyl probably constitutes the most serious environmental hazard of the nickel alloys and compounds that have been studied. This toxic and readily volatile compound is used both for the preparation/recovery of nickel and as a catalyst in carbonylation reactions that have gained wide commercial acceptance. Assuming a pound loss of catalyst for each ton of end product in a carbonylation reaction, about 24 tons of nickel carbonyl per year might be consumed in the process - a source of contamination to man and the atmosphere. A new, multifunctional gasoline additive - nickel isodecylorthophosphate - deserves scrutiny as a possible environmental (atmosphere) hazard, especially if the large anticipated uses are realized.

Nickel Toxicity

Depending on the organism and the type of compound, nickel can be beneficial or toxic. Injected nickel, especially as nickel carbonyl, is very toxic. Carcinogenecity on exposure to nickel carbonyl has been found in some industries.

Systemic poisoning from nickel salts is almost unknown from both therapeutic and industrial usage. Nickel dermatitis has been reported in industrial workers, especially nickel platers and cement workers, and its incidence appears to be rising.

Orally administered nickel is excreted mainly in the feces and injected nickel in the urine. The chief storage depots of administered nickel are the spinal cord, brain, lungs, and heart.

The toxicity of nickel is believed to be due to its capacity to inhibit enzyme systems.

Symptoms of acute poisoning with nickel, especially nickel carbonyl, are an initial attack of headache, dizziness, nausea, and vomiting with a delayed syndrome of chest and respiratory complications that in some cases results in death. Elevated blood and urine median values of 30 μg/l and 7.4 μg/l, respectively, have been reported. The concentration of nickel in the urine remains high for at least 24 hours after exposure to nickel carbonyl and can possibly be correlated with the severity of exposure. If acute poisoning is not lethal, treatment with sodium diethyldithiocarbamate is effective.

Environmental Nickel

The average and maximum concentrations of nickel monitored in the National Air Sampling Network of the Public Health Services during 1964 and 1965 were 0.034 and 0.50 $\mu g/m^3$, respectively. The 1960 and 1961 monitoring by the National Water Quality Network of the Public Health Service gave nickel contents ranging from 0.001 to 0.07 mg/l.

The presence of nickel in some tobacco smokes has been reported. An estimate of the quantity of nickel that would be inhaled annually by a heavy smoker of such tobaccos gives a value that is carcinogenic in some animals.

According to a Russian report, the maximum permissible concentration of nickel in drinking water is 1.0 mg/l. The safe limit does not seem to be established for United States standards.

Recommendations

Our analysis of the environmental influence of nickel suggests that usage of this metal and its compounds is growing in many applications. Monitorings by both the National Air Sampling Network and the National Water Quality Network indicate widespread dissemination of nickel in our environment. However, to our knowledge, it is not known whether nickel at the concentrations present in air and water constitutes an environmental hazard to man. Therefore, the following recommendations are made:

(1) Based on the levels of nickel that are currently being monitored in our environment, research should be initiated to determine the chronic effects of nickel in animals, in hopes of establishing concentration levels at which it may affect man.

(2) The chronic effects of small quantities of nickel in food should be determined. This need is premised on the use of large quantities of nickel equipment in food processing, with transfer of some nickel to the product during processing.

SECTION 4. ENVIRONMENTAL HAZARDS OF FLUOROCARBONS

Production and Consumption

About ten companies in the United States, with an annual capacity of 600 million pounds, are engaged in the production of fluorocarbons. Techniques for the manufacture of these materials include the fluorination of hydrocarbons, the electrolysis of solutions of alcohols, acids, or amines in anhydrous hydrogen fluoride, the pyrolysis of saturated chlorofluorohydrocarbons, and the reaction of anhydrous hydrogen fluoride with acetylene.

The production of plastics and resins from fluorochemicals is based upon the polymerization and copolymerization of unsaturated compounds.

Use Pattern

Fluorochemicals of concern in this study are used as aerosol propellants, refrigerants, foam-blowing agents, resins, plastics, solvents, dielectric fluids, degreasing fluids, and pharmaceuticals. About 85 to 90 percent of the usage is in aerosols, refrigerants, plastics, and resins.

Fluorochemical aerosols are used primarily in shaving creams and colognes. The only FDA-cleared fluorocarbon propellants for foods are Freon C-318 and Freon 115. Food aerosols at present are generally propelled by compressed soluble gases - carbon dioxide, nitrous oxide, and nitrogen. Conceivably, fluorocarbon aerosols might penetrate the market for such food aerosol products as sauces, frostings, spreads, flavorings, and seasonings.

Generally, saturated fluorochemicals, e.i., fluorocarbons 11, 12, 22, 113, and 114, are used in household and commercial refrigeration and air conditioning.

A potentially large use for fluorochemicals is the coin-operated, dry-cleaning-solvent market. If this truly takes hold, it could serve as a multimillion-pound outlet for fluorochemicals.

Several fluorochemicals have been used as general anesthetics.

Fluorocarbon Toxicity

Most saturated fluorocarbons are relatively nontoxic. In test cases with perfluorobutane and perfluorocyclobutane with 20 percent oxygen, rats exposed for 4 hours showed only slight effects on respiration, but no pathological changes in organs. On the other hand, the toxicity of unsaturated compounds increased directly with the fluorine, chlorine, and bromine content. The relation between fluorine content and unsaturation is shown in the following tabulation in which rats were exposed for 4 hours:

Compound	LC_{50}, ppm by vol
Vinyl Fluoride, CH_2=CHF	800,000
Vinylidene Fluoride, CH_2=CF_2	128,000
Tetrafluoroethylene, CF_2=CF_2	40,000
Hexafluoropropylene, CF_3-CF=CF_2	3,000
Perfluoroisobutylene, $(CF_3)_2C$=CF_2	0.5

The local effects of fluorocarbons may produce very mild irritation of the upper respiratory tract. Systemically, some of the fluorocarbons may produce mild central-nervous-system depression, possibly due in part to displacement of air, with resultant hypoxia. Thermal-decomposition products of fluorocarbons may cause severe irritative effects. Generally, anesthetics based on fluorocarbons do not produce significant adverse results. Traces of unsaturates in anesthetics, however, can lead to sharp increases in toxicity.

Under ordinary conditions, the fluorocarbon plastics are nontoxic. However, inhalation of, for example, Teflon dust can lead to "polymer fever". Products from the incomplete combustion of fluorocarbons are toxic because of the presence of unsaturates, partially oxidized, halogenated, or fluorinated fragments.

Environmental Fluorocarbons

The environmental hazards due to fluorocarbons have not been considered to any extent in the literature. Many of these compounds are stable and relatively safe at ordinary temperatures but have very dangerous pyrolysis products. With 600 million pounds per year of these compounds being cycled through the industrial "mill" to reach the public, it should be of concern to evaluate how much and in what form these materials reach the open environment. Industrial wastes should be important. Incineration products, perhaps from disposal of scrap fluoroplastics, should be especially examined.

If it is found that large quantities of these wastes are entering the atmosphere and streams, the toxic effects of these materials will have to be studied and maintained within acceptable limits.

Recommendations

The results of this study substantiate the wide use of fluorocarbons in industry. In order to arrest or eliminate the environmental hazards that might result from their industrial applications, the following recommendations are made:

(1) Additional research is needed to determine the thermal-degradation products of fresh and aged fluoroplastics and the toxicological characteristics of these products.

(2) The volatility of the well-known industrial fluorocarbons suggests the need for the establishment of base and safety levels of fluorine compounds in the environment.

(3) The potential use of fluorocarbons as food propellants in pressurized containers required proof that the compounds would be safe for humans ingesting them in foods. As new fluorocarbons find their way into the food propellant's market, toxicity studies commensurate with the hazards involved need to be initiated.

(4) Further refinement and control of analytical techniques are required to detect traces of contaminants – specifically, unsaturated compounds in fluorocarbon formulations. This need is especially critical in anesthetic formulations.

SECTION 5. ENVIRONMENTAL HAZARDS OF PULP AND PAPER CHEMICALS

Production and Consumption of Paper Products

The production of some 47 million tons of paper products during 1966 was a record high for the paper industry in the United States. The rate of use of paper and packaging products was estimated at 510 pounds per capita; 10 years ago, the figure was 412 pounds.

Use Pattern

Hundreds of pulp and paper mills, distributed throughout 44 of the 50 states, are engaged in pulp processing, pulp bleaching, and paper and paperboard manufacture. These three operations involve the consumption and conversion of some millions of tons of inorganic and organic chemicals annually. The use of pulp and paper chemcials is expected to increase at a rate of 5 percent per year. These increases will be accommodated by the expansion of established processes and by the application of new processes using different types of chemical treatments.

Pulp manufacture uses such basic chemicals as salt cake, chlorine, lime, sulfur, caustic soda, sodium sulfite, and ammonia. Chemicals used in pulp bleaching are chlorine, sodium chlorite, sodium hypochlorite, hydrogen peroxide, and zinc hydrosulfite. Chemicals employed in paper and paperboard manufacture include cornstarch, alum, rosin sizing, titanium dioxide, calcium carbonate, wax sizing, latexes, wet-strength resins, casein, clay, dyes, optical brightening agents, and retention aids. This market has developed rapidly during the last decade.

Pulp and Paper Chemicals Toxicity

Threshold limits of exposure have been established for some of the sulfur-containing atmospheric pollutants from the pulp and paper industry. These and their limits in animal studies are:

Agent	Threshold Limit, mg/m^3
Hydrogen sulfide	28
Methyl mercaptan	100
Sulfur dioxide	13

Threshold limits on methyl sulfide and dimethyl disulfide could not be located.

Of the polyaromatic hydrocarbons that are adsorbed by salt cake entrained in the flue dust of recovery furnaces, benzo[a]pyrene is commonly referred to as a strong carcinogen. However, quantitative data are lacking concerning its carcinogenicity under conditions comparable to emissions in stack gases.

In many cases, especially those involving the use of organic additives, no standards for limits have been determined.

Environmental Inputs From Pulp and Paper Chemicals

By-products are formed and processing losses occur during the whole sequence of paper-making operations, so that a variety of environmental inputs may occur. The pulping operation induces a preferential chemical degradation, solubilization, and partial removal of the lignin binder of the wood, so that the wood fibers can be separated and reformed into paper. Lignin represents about 25 percent of the original wood. Although it must be removed, it has no large-scale use commensurate with the tremendous quantities produced, so that disposal of the sulfur-containing lignins is a problem that can impose environmental burdens.

The separated wood fibers carry with them some colored constituents and lignin residues that must be decolorized with bleaching agents, which in turn form by-products during the bleaching process. These may contaminate water or the atmosphere. Thus, pulping and bleaching operations lead to the formation of a number of materials that may become environmental hazards to man. These include such volatiles as sulfur dioxide, hydrogen sulfide, methyl mercaptan, dimethyl sulfide, dimethyl disulfide, chlorine, chlorine dioxide, methanol, ethanol, acetone, methyl isobutyl ketone, α-pinene, β-pinene, Δ^3-carene, camphene, limonene, cineole, and α-terpineol.

The alkaline cooking process for production of kraft pulp would be economically unattractive if the alkali could not be recovered and reconstituted for reuse. Commonly, the waste liquor is collected and evaporated, and the lignin materials are burned out of the solid residue in recovery furnaces to separate them from the incombustible alkali salts. The flue gases inevitably carry out some entrained salt particles and some volatile organic decomposition products formed during combustion. Polyaromatic hydrocarbons condensed out in the flue gases or adsorbed on the salt-cake particles discharged from recovery furnaces have been identified as: benzo[a]pyrene, benzo[e]pyrene, benzo[g, h, i]perylene, chrysene, coronene, fluoranthene, and pyrene.

Many of the chemicals listed above as being used in paper and paperboard manufacture are additives that are incorporated into the paper web, when it is formed, by adding them to the fiber suspension before it is fed to the paper machine. Some of the chemical additive unavoidably remains in the water draining from the paper machine as effluent, and enters the environment. Paper chemicals are also used in coating mills, which apply opacifying and finishing coats to one or both sides of a preformed paper web. Wastes from coating processes are usually uneconomical to reprocess and are difficult to dispose of. Slurries may be impounded in storage ponds or thickened and discarded into landfills. They may be dispersed inadvertantly by leakage or by surface waters. The organic sizes and resins may be converted to noxious gases and soluble products by bacterial action, thus entering the environment as secondary contaminants.

Recommendations

Our analysis of the pulp and paper industry suggests a number of sources of environmental contamination. Health hazards from concentrations of gases found in the area around sulfate pulping operations are not considered to be of serious consequence.

However, little is known about the true air-pollution signatures of sulfate pulping. Therefore, the following recommendations are made:

(1) We need to know what chronic low-level exposure damage is possible from sulfur-containing materials. Although no disease or infirmity seems to be directly caused by odors per se in the vicinity of pulping operations, we do not have base-line data.

(2) The possible deleterious effects in the environment of polynuclear hydrocarbons needs to be investigated. If carcinogens are released, corrective measures must be taken to remove them from the environment or to prevent their generation in mill operations.

(3) Continuous surveillance of paper additives, e.g., dyes, sizing agents, and water- and oil-resistant agents should be maintained to determine whether these additives constitute an environmental hazard. If the results are positive, the need will arise to establish base levels of safety. This calls for new analytical techniques and the establishment of toxicological parameters.

(4) An examination of terrestrial sources as possible sources of contaminants in paper is suggested. This need is supported by the recent observation by Dr. P. W. West of Louisiana State University (Chem. Eng. News, May 29, 1967, p 12) that selenium found in cigarette paper and to a significant degree in most other kinds of paper, may be an important cause of lung cancer and emphysema.* The selenium is concentrated in vegetation, which in turn is used in making paper. Conceivably, other environmentally hazardous materials might be concentrated in plants or trees and show up in paper during pulping.

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*Selenium is monitored by the National Water Quality Network of the Public Health Service.

APPENDIX A

MERCURY

APPENDIX A

MERCURY

Economics Information

Natural Occurrence(A-1, A-2)*

Mercury is commonly found as the sulfide (HgS), frequently as the red cinnabar, and less often as the black metacinnabar. Important deposits are located in Spain, Italy, California, Nevada, Alaska, Oregon, Texas, Mexico, Canada, Brazil, Peru, China, Japan, Russia, Hungary, Yugoslavia, and Germany. A less common ore is the mercury (I) chloride found in Texas.

The reserves of mercury at Almadén, Spain, have been estimated at 40,000 tons; those in Idrea, Italy, at about 20,000 tons. The ore found in Spain has the highest mercury content, with an average of 0.5 to 1.2 percent Hg, sometimes as much as 10 percent Hg. It has been estimated that the outer, 16-km-thick layer of the earth's crust contains 2.7×10^{-6} percent Hg. The oceans contain 3.0×10^{-9} percent, or approximately 50 million metric tons of mercury.

Domestic Production and Reclamation(A-3, A-4, A-5)

Primary Sources. Domestic primary production of mercury in the United States during 1966 rose for the second consecutive year. However, of 80,000 flasks of mercury consumed in 1966, only 22,000 flasks were produced from domestic deposits.

During 1965, California was, as usual, the leading mercury-producing state, supplying 69 percent of the domestic total. Nevada was in second place, supplying 17 percent. The remainder of the 1965 production, 14 percent, was furnished by Alaska, Arizona, Idaho, Oregon, Texas, and Washington. The following five mines supplied about 75 percent of the total domestic output in 1965, each mine producing more than 1,000 flasks:

State	County	Mine
California	San Benito	New Idria
Ditto	San Luis Obispo	Buena Vista
"	Sonoma	Mt. Jackson
Idaho	Washington	Idaho-Almadén
Nevada	Humboldt	Cordero

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*References for Appendix A will be found on p A-34.

Mines producing 100 flasks or more were as follows:

State	County	Mine
Alaska	Aniak district	White Mountain
California	Marin	Gambonini
Ditto	San Benito	Aurora
"	Santa Barbara	Sun Bird (Gibralter)
"	Santa Clara	Guadalupe
"	Santa Clara	New Almadén
"	Shasta	Welty
"	Sonoma	Culver Baer
"	Sonoma	Socrates
Nevada	Esmeralda	B & B
Ditto	Nye	Ione Mercury
"	Pershing	Kitten Springs
Oregon	Lane	Black Butte
Oregon	Malheur	Bretz

These 19 mines accounted for approximately 95 percent of the domestic primary output.

Table A-1 gives the quantity of mercury produced in the United States during 1964 and 1965 according to state and the value of the mercury produced. Table A-2 presents the quantities of ore treated and the mercury produced in the United States from 1956-1965.

TABLE A-1. MERCURY PRODUCED IN THE UNITED STATES BY STATE DURING 1964 AND 1965

State	Producing Mines	Flasks(a)	Value(b), thousands of dollars
	1964		
Alaska	3	303	95
Arizona	4	77	24
California	39	10,291	3,240
Idaho	1	83	26
Nevada	21	3,262	1,027
Oregon	4	126	40
Total	72	14,142	4,452
	1965		
Arizona	7	158	90
California	84	13,404	7,650
Idaho	2	1,119	639
Nevada	42	3,333	1,902
Oregon	7	1,364	779
Alaska, Texas, and Washington	7	204	116
Total	149	19,582	11,176

(a) Flask = 76 lb.

(b) Value calculated at average New York price.

TABLE A-2. MERCURY ORE TREATED AND MERCURY PRODUCED IN THE UNITED STATES[(a)]

Year	Ore Treated, short tons	Mercury Produced Flasks	Pounds Per Ton of Ore
1956-60 (average)	283,182	31,918	8.6
1961	262,108	31,633	9.2
1962	146,523	26,228	13.6
1963	113,539	19,101	12.8
1964	149,950	14,115	7.2
1965	339,124	19,353	4.3

(a) Excludes mercury produced from placer operations and from cleanup at furnaces and other plants.

During 1964, about 90 percent of the primary production of mercury in the United States came from underground sources in which about 5 tons of ore were handled per man shift. Ores averaged 7 or 8 pounds of mercury per ton. The remaining 10 percent of primary production was open-pit mining, in which up to 40 tons of ore were processed per man shift. These ores averaged about 3 pounds of mercury per ton. During 1965, primary mining operations included the use of ores averaging 4.3 pounds of mercury per ton of ore.

It can be anticipated that the law of supply and demand for mercury may require mining of ores less rich in mercury than have been used for domestic primary production. This circumstance may require the development of new or inactive mines and subsequent control of the hazards associated with the production of mercury. Estimates have been compiled of domestic resources of mercury producible at various price ranges for each mercury mine. This information was obtained by combining specific knowledge of mercury mineralization with estimates of potential based on geologic information and past production history. A parallel estimate is available of nationwide production potential based on a study of past price and production relationship.

In present mining operations, all active working levels are interconnected so that natural/fan ventilation can be achieved. Dead-end workings, particularly raises and stopes, are equipped with secondary ventilation systems to remove smoke and gases and supply men with the legal minimum of 2000 cfm of fresh air per man. Safety conditions are controlled by the mine foreman and the manager and are under surveillance by the state mining inspector and the engineer for the insurance company. Operations are inspected at least once a month.

Secondary Sources. Production of secondary mercury rose to 45,698 flasks in 1965, largely as a result of the release of 29,753 flasks of AEC mercury. Recovery of secondary mercury from commercial sources was at the highest level since 1947, when data were first collected. It was approached only by 1958 production of 10,300 flasks. Sources of secondary mercury during 1965 were reclaimed dental amalgams, oxide and acetate sludges, battery scrap, and a decommissioned mercury boiler.

Annual production of secondary mercury in the United States from 1960 to 1965 was:

Year	Flasks
1960	5,350
1961	8,360
1962	5,800
1963	10,520
1964	23,780
1965	45,700

Refining.(A-6) With the gradual depletion of the higher-grade ores, concentration of low-grade mercury ores prior to roasting or leaching is assuming new and more importance. Methods of beneficiating mercury ores include hand sorting, crushing and screening, jigging, tabling, and flotation. Of these methods, flotation is the most efficient for beneficiating mercury ores and produces 25 to 50 percent concentrates with mercury recoveries of about 90 percent and with the weight of the flotation concentrate less than 1 percent of the original feed.

Only the Hermes plant in Idaho, constructed in 1957, employs leaching. Crude cinnabar is leached with caustic solution to remove the arsenic. The cinnabar concentrate is then treated with a caustic-sodium sulfide solution to remove 99 percent of the mercury. Mercury is recovered from solution by electrolytic precipitation. The recovery of mercury from ore and concentrate by roasting has been the principal method of refining mercury. Involved is a distillation process that consists essentially of heating the cinnabar to volatilize the mercury, followed by condensation of the mercury vapor. Either mechanical furnaces (multiple hearth or rotary) or retorts are used to roast mercury-bearing materials. Furnacing is a continuous operation, whereas retorting is a batch operation. Except for the type of furnace used, mercury-recovery plants are essentially the same. Each plant has facilities for storing, crushing, conveying, and feeding ore, a furnace, a dust collector, a condensing system, a gas fan, a gas tower and stack, a calcine bin, a hoeing machine, bottling equipment, an apparatus for regulating and controlling pressures and temperatures throughout the plant, assaying facilities, and cleaning and purification systems.

With careful control of properly designed plants, mercury recovery employing furnace roasting averages 95 percent or more. The major loss of mercury occurs in the stack gases, with minor losses in the calcine, dust, and spillage. Retorts are slightly more efficient than furnaces, and mercury recovery usually exceeds 98 percent.

Domestic suppliers of primary- and secondary-source mercury are the following:

Primary

Associated Metals & Minerals Corporation, New York
Ayrton Metal & Ore Corporation, New York
Bache & Company, Incorporated, New York
Belmont Smelting & Refining Works, Incorporated, Brooklyn, New York
Brandeis, Goldschmidt & Company, Incorporated, New York
Browning Mineral & Ore Company, New York
Colton Metalex Company, Los Angeles, California
Goldsmith Division of National Lead Company, Chicago, Illinois
W. R. Grace & Company, New York
K. Hettleman & Sons Division, Minerals & Chemicals Philipp Corporation, Baltimore, Maryland
Intercontinental Metal Corporation, New York
International Minerals & Metals Corporation, New York
International Selling Corporation, New York
Fred H. Lenway and Company, Incorporated, San Francisco, California
Leytess Metal & Chemical Corporation, New York
Lorch Metal Corporation, New York
Mercer Alloys Corporation, Greenville, Pennsylvania
Metalchemical Commercial Corporation, New York
Metal Traders, Incorporated, New York
Miles Metal Corporation, New York
Philipp Brothers, New York
Shepard Chemical Industries, Incorporated, New York
Simmons Refining Company, Chicago, Illinois
Spiral Metal Company, Incorporated, South Amboy, New Jersey
United Refining & Smelting Company, Chicago, Illinois

Secondary (Redistilled)

Bache & Company, Incorporated, New York
Browning Mineral & Ore Company, New York
Goldsmith Division of National Lead Company, Chicago, Illinois
K. Hettleman & Sons Division, Minerals & Chemicals Philipp Corporation, Baltimore, Maryland
International Minerals & Metals Corporation, New York
Lorch Metal Corporation, New York
Martin Metals, Incorporated, Los Angeles, California
Shepard Chemical Industries, Incorporated, New York
Simmons Refining Company, Chicago, Illinois
United Refining & Smelting Company, Chicago, Illinois

Use Pattern[(A-4)]

Although there have been fluctuations during the last decade in the quantities of mercury consumed in specific industrial categories, there have been no additions or deletions of categories. This suggests that mercury consumed in the United States could conceivably peak at about 80,000 flasks per year, the quantity used in the United States during 1966. A breakdown of the use pattern for 1956 through 1965 is given in Table A-3.

TABLE A-3. MERCURY CONSUMED IN THE UNITED STATES BY USES

Flasks

Use	1956-60 (Average)	1961	1962	1963	1964	1965
Agriculture (including fungicides, and bactericides for industrial purposes)	7,311	2,557	4,266	2,538	3,144	3,116
Amalgamation	250	278	299	306	667	495
Catalysts	906	707	874	612	656	924
Dental preparations[(a)]	1,610	2,154	2,033	2,346	2,612	1,619
Electrical apparatus[(a)]	9,285	10,255	11,564	11,115	10,690	14,764
Electrolytic preparation of chlorine and caustic soda	4,792	6,056	7,314	7,999	9,572	8,753
General laboratory use:						
Commercial	1,052	1,484	1,752	1,241	1,516	2,827
Government	--	--	--	3,821	17,000	--
Industrial and control instruments[(a)]	6,177	5,627	5,186	4,943	4,972	4,628
Paint:						
Antifouling	1,913	915	124	252	547	255
Mildew proofing	NA[(b)]	5,146	4,554	6,403	4,898	7,534
Paper and pulp manufacture	NA	3,094	2,600	2,831	2,148	619
Pharmaceuticals	1,645	2,515	3,378	4,081	5,047	3,261
Redistilled[(a)]	9,329	9,013	8,987	9,227	11,405	12,257
Other	8,673	5,962	12,370	20,248	7,734	15,402
Total	53,143	55,763	65,301	77,963	82,608	76,454

(a) A breakdown of the "redistilled" classification showed ranges of 45 to 38 percent for instruments, 21 to 8 percent for dental preparations, 44 to 25 percent for electrical apparatus, and 18 to 8 percent for miscellaneous uses in 1956-64, compared with 45 percent for instruments, 15 percent for dental preparations, 19 percent for electrical apparatus, and 21 percent for miscellaneous uses in 1964.

(b) Not available.

Industrial consumption of mercury rose about 17 percent in 1965 over 1964, but total consumption was lower because 1964 consumption included 17,000 flasks distributed to Government agencies from surplus AEC material. The larger industrial consumption was due largely to demand generated by new or expanded caustic soda-chlorine plants, requiring mercury cells.

In addition to the increase in the use of mercury in the mercury cell, increases also were noted in the following categories:

Use	Percent
Catalysts	41
Electrical apparatus	38
Commercial laboratory use	86
Mildewproofing (paints)	54
Redistilled	7

Declining use was shown in these categories:

Use	Percent
Agriculture	<1
Amalgamation	26
Dental preparations	38
Industrial and control instruments	7
Antifouling (paints)	53
Paper and pulp manufacture	71
Pharmaceuticals	35

Mercury-Cell Chlorine Production. (A-7 - A-10) Four mercury-cell caustic-soda chlorine plants came on stream in 1965. There were also two plant expansions. Consumption data for new plants and expansions are included under "other" uses in the above compilation of use categories.

New caustic-soda chlorine plants using the mercury-cell process and expansions of existing plants in 1965 were:

Company	Location
Detrex Chemical Industries, Incorporated	Ashtabula, Ohio*
Diamond Alkali Company	Delaware City, Delaware
The Dow Chemical Company	Plaquemine, Louisiana*
Georgia-Pacific Corporation	Bellingham, Washington
Olin Mathieson Chemical Corporation	Augusta, Georgia
Stauffer Chemical Company	Le Moyne, Alabama

*Plant expansion.

According to the United States Bureau of Mines, 80,000 flasks of mercury were consumed in the United States in 1966. This compares with 76,454 flasks in 1965. The increase over 1965 is reflected primarily in the construction of additional chlorine-caustic soda plants using a mercury-cell process. In 1966, 10,300 flasks were used, compared with 8,753 flasks in 1965. About 13,000 additional flasks were used in 1966 to charge cells in new plants and expansions.

In 1966, 7.1 million tons of chlorine were produced by all processes. It is estimated that by 1970, 10 million tons total will be produced. About 3.0 million tons of total chlorine production in 1970 will be produced by mercury-cell plants. Since each ton of chlorine production consumes about 0.4 pound of mercury, about 16,000 flasks will be consumed annually by 1970 in the electrolytic production of mercury. This amounts to about 44 flasks (3,300 pounds) per day. Conceivably, this could be a source of mercury contamination.

As electrolytic chlorine plants come on stream, additional mercury consumed to charge the new mercury cells will aggregate between 47,000 and 60,000 flasks through 1970. This inventory buildup contributes to the currently rising demand for mercury, and the projections of new or expanded mercury-cell chlorine plants are already playing havoc with prices. Undoubtedly there will be adjustments in use patterns as prices continue upward. In June, 1966, mercury was selling for about $330/flask; in December, 1966, $580/flask; in February, 1967, $500/flask. Some sources predict that prices will reach $1,000/flask. There is no indication that the chlorine producers are retreating from their plans to expand electrolytic chlorine-producing plants. For example, General Aniline announced a planned expansion of its Linden, New Jersey, facilities for chlorine production using a BASF-Krebs electrolytic cell.(11)

Rising prices for mercury may stimulate increases in both United States production and imports and may also lead to two prices for mercury for mercury cells – one for makeup to replenish losses at the going market price and lower-than-market price for initial inventory. Until the supply and demand again approach a balance, mercury very likely will remain in short supply and will be expensive. Mercury will certainly continue to be a target for replacement by substitutes in many use patterns. These factors must be considered in delineating the use patterns of mercury in areas besides the mercury cells. Some of the more significant of these areas of consumption are discussed below.

Apparatus, Instruments, and Related Uses.(A-12 – A-14) The largest single use for mercury that is shown individually in the use compilation, 14,764 flasks, is "Electrical Apparatus". Many of these items also overlap with those under the headings "General Laboratory Use", and "Industrial and Control Instruments". For convenience, subcategories of instrument and control apparatus are listed below and a few of the less familiar electrical uses of mercury are discussed briefly in this section.

Apparatus and instruments uses for mercury are as follows:

Thermometers
Hygrometers (measurement of dew point)
Manometers (pressure gages for all gases)
Compensating clock pendulums
Barometers (a type of manometer)
Weightometers
Vacuum gages
Tank gages
Flowmeters (water, sewage, steam, compressed air, high-pressure gases)
Gyroscopes
Switches, relays, fuses
Standard cells
Reference electrodes
Batteries
Light sources
Arc rectifiers, oscillators (for electric furnaces)
High-vacuum diffusion pumps (originally for radio, TV tubes, neon tubes)
Electric-motor clutches and seals

Memory units for electronic computers
Power-control switches for motors.

Standard cells are exemplified by:

(1) The Clark cell, constructed around one electrode of mercury, another electrode of an amalgam of zinc and mercury, and a saturated solution of zinc sulfate

(2) The Weston cell, which contains electrodes of mercury and of cadmium, and a saturated solution of cadmium sulfate for an electrolyte.

The mercury gyroscope is used for automatic guidance of vehicles. It does not provide any market for mercury. It consists of only a small, sealed, fused-quartz vial that contains the nuclei of two different mercury isotopes that are instrumented to measure and correct any change in direction of the vehicle.

In a reference electrode, a normal potassium chloride solution that is saturated with mercurous chloride generates a constant, known voltage difference when it is in contact with elemental mercury. A cell can be constructed with a mercury electrode, an electrolyte of the composition mentioned above, and some material for the other electrode.

Mercury-vapor lamps came into wide use by the second half of the twentieth century. The high-pressure lamps are suitable for photochemical and general purposes. They are operated under higher voltages than conventional lamps, and they deliver more lumens per watt of energy consumed. Mercury lamps are used extensively for street and highway lighting, in high-ceilinged rooms, and where intensive lighting is needed for motion-picture projection, in photography, for examination of teeth, heat lamps, and water sterilization. It has been reported that Westinghouse Electric Corporation alone purchases from 15,000 to 20,000 pounds of mercury annually, mostly for lamps. An electric discharge through mercury vapor generates light rich in ultraviolet rays that is useful in sunlamps and for therapeutic purposes. Mercury vapor enclosed in quartz tubes is used similarly as the current conductor in arc rectifiers and oscillators.

The mercury battery is a comparatively new type of small dry cell. The positive electrode is a mixture of graphite and mercuric oxide, and a powdered zinc-mercury alloy is the negative electrode. These are separated by a composite shield that contains an electrolyte of potassium hydroxide and zinc oxide. These mercury cells have been used mainly as power supplies for many types of transistorized devices, ranging from hearing aids to missile-guidance systems, especially where miniaturization is required, e.g., power packs for radio transmission of data from the first United States satellites, Geiger counters, portable radios, communications equipment, electronic measuring devices, digital computers, and temperature-detection devices. While only small amounts of mercury are used for each cell, large numbers of units are made each year, and a moderate increase in the mercury consumed can be anticipated. Approximately 30 million cells valued at 30 million dollars are currently manufactured.

Apparatus, instruments, and related uses of mercury are distributed throughout the United States. Therefore, it is useful to know who manufactures, distributes, and services instruments and equipment premised on mercury - for example, thermometers, manometers, barometers, standard cells, reference electrodes, and light sources.

This information can be obtained from the 1966 Laboratory Guide to Instruments, Equipment, and Chemicals.(12)

Paint.(A-15-A-17) Antifouling Agents. Consumption in 1965 was 255 flasks compared with 547 flasks for 1964 and an annual average of 1913 flasks for the period 1956 to 1960. Small quantities of mercuric oxide (yellow and red), mercuric sulfide as antifouling agent, and miscellaneous organic mercurials, e.g., phenyl mercury naphthenate and phenyl mercury hydroxide, are used in antifouling paints. This market, however, is being captured by either more economical or less toxic materials - for example, tributyl tin oxide, tributyl tin oxide esters, triaryl bismuth and triaryl boron, cuprous oxide and cuprous oxide/sodium silicate, copper 8-hydroxyquinolinate, tributyl lead acetate, zinc chromate, metal chelates of acetoacetic ester, and fluorinated phenarsazine. Manufacturers and distributors of active ingredients used in antifouling paint formulations based on mercury include:

Allied Chemical Corporation, General Chemical Division
American Firstoline
Atomergic Chemical Metals
J. T. Baker Chemical Company
W. A. Cleary Corporation
Electronics Space Products
D. F. Goldsmith Chemical and Metal
H. Kohnstamm and Company
Mallinckrodt Chemical Works
McKesson & Robbins, Incorporated
Metasol Products
Robeco Chemicals, Incorporated
Rocky Mountain Research, Incorporated
Steritized, Incorporated
Troy Chemicals
Wood Ridge Chemicals

Mildewproofing Agents.(A-18 - A-20) In contrast to the rapid decline in the use of mercury compounds as antifouling agents in paints, mildewproofing applications showed a spectacular rise during 1965, when 7,534 flasks of mercury were consumed compared with 4,898 flasks in 1964. Most of the gains in 1965 were attributable to the phenyl mercurials, for example:

Phenyl mercury
Phenylmercuric acetate
Phenylmercuric ortho benzoic sulfimide
Phenylmercuric borate
Phenylmercuric chloride
Phenylmercuric hydroxide
Phenylmercuric oleate
Phenylmercuric naphthenate
Phenylmercuric propionate
Phenylmercuric salicylate
Phenylmercuric stearate
Phenylmercuric dimethyldithiocarbamate
Di(phenyl mercury)dodecenyl succinate.

Phenylmercuric oleate, propionate, and the acetate are of major importance. The acetate is used in self-cleaning outdoor paints. The acetate, oleate, and succinate are used primarily for mildew resistance and preservation of alkyd paints in polyvinyl acetate and acrylics. They cannot be used with sulfur-based pigments since they will discolor, nor should they be used with aluminum. The salicylate is used as an antimicrobial agent for urea formaldehyde resins; the acetate, salicylate, and stearate in phenolic polymers; and organic mercurials in general for polyvinylidene chloride coatings.

Although the use of organic mercurials for mildewproofing of paints and plastics showed a rapid increase during 1965, a long-range prediction indicates a decline in their use. Compounds of tin and boron look like replacements.

Manufacturers and distributors of mildewproofing organic mercurials include:

Advance Division, Carlisle Chemical Works
W. A. Cleary Corporation
H. Kohlstamm and Company
Merck Chemistry
Metasol Products
Naftone, Incorporated
Nuodex Products Company
Stecker Chemicals
Steritized, Incorporated
Troy Chemicals
Vineland Chemicals
Wood Ridge Chemicals

Agriculture.(A-21 - A-24) The 1965 consumption of 3,116 flasks includes fungicides and bactericides for industrial applications as well as for agriculture. Since there is considerable overlap among agricultural, paint, and pharmaceutical uses, categorization becomes a matter of judgment.

A comprehensive compilation for agricultural uses of mercurial chemicals is found in Frear's Pesticide Handbook. Included in this compilation are approximately 130 organic and inorganic mercurials in such categories as fungicides, herbicides, insecticides, and rodenticides. The book is divided into three sections. Section I lists all trade names of commercial pesticides and equipment in alphabetical order, without regard for the type of production. Each product is identified by a number preceding the trade name. In Section II, all products are arranged according to use in some 30 categories - for example, fungicide dusts, fungicide sprays, granular insecticides, and seed treatments. In Section III, the names and addresses of all manufacturers are arranged in alphabetical order, followed by the reference numbers of the products manufactured by each of them. By locating these reference numbers in Section I, all of the trade names of the products made by any manufacturer can be obtained.

Since the production figures generally do not correspond to 100 percent formulations, there isn't any correlation between flasks of mercury consumed in the agricultural category and the quantity of pesticide manufactured. For example, in 1964, production of phenylmercuric acetate was 495,000 lb. On a stoichiometric basis, this would have required 3,870 flasks of mercury. Since only 3,144 flasks of mercury were reportedly used in 1964 for agricultural purposes, the figure can only serve as a guideline. Apparently, the largest outlet for organic mercurials is phenylmercuric acetate as a fungicide and herbicide. The other organic mercurials are lumped in the 1964 statistics at 1,138,000 lb. It is believed that the 1966 production figures for organic mercurials, including phenylmercuric acetate, have not changed much from the 1964 reported values.

Frear does not give production figures for inorganic mercurials, but does identify formulations containing inorganic mercurials such as mercuric chloride, mercurous chloride, and mercuric oxide as fungicides. The *Farm Chemicals Handbook* also lists basic producers, formulators, and distributors of inorganic mercurials and, to a limited degree, of organic mercurials. Chemical Week, Buyers Guide Issue, 1967, Chemicals, contains a general listing of organic and inorganic mercurials in addition to manufacturers and distributors.

Based on data reported in the above publications, it is believed that the key inorganic and organic mercury compounds for agricultural uses are:

Inorganic

Mercuric acetate
Mercuric chloride
Mercurous chloride
Mercurous nitrate
Mercuric oxide (red and yellow)

Organic

Phenylmercuric acetate
Phenylmercuric benzoate
Phenylmercuric borate
Phenylmercuric chloride
Phenylmercuric cyanide
Phenylmercuric dithiocarbamate
Phenylmercuric hydroxide
Phenylmercuric lactate
Phenylmercuric nitrate
Phenylmercuric oleate
Phenylmercuric propionate
Phenylmercury salicylate
Selected amine salts of phenyl
  mercurials
Ethylmercuric acetate
Ethylmercuric chloride
Ethylmercuric phosphate
Methylmercuric hydroxide.

The major uses of mercury in the field of agriculture are in formulas for pesticides. These pesticides are listed in Table A-4.

Pharmaceuticals.(A-24 - A-29) In 1964, consumption of mercury in pharmaceuticals was 5,047 flasks. This decreased to 3,261 flasks in 1965. Doubtless, such factors as economics and toxicological regulations played a role in this decline. Also, benzothiadiazines are showing rapid gains in the market for diuretics.

The major uses of mercury in pharmaceuticals are in the fields of diuretics and antiinfectives (antiseptics). Major types of each of these mercurials are identified in Tables A-5 and A-6, respectively.

In addition to the above antiinfectives, information is available on the use of specific phenyl mercurials for the manufacture of such formulations. These include:

TABLE A-4. MERCURY-CONTAINING PESTICIDES

Commercial or Trade Name	Active Mercury Ingredient	Manufacturer/Distributor/ Formulator
Acme Panogen	Methyl mercury dicyandiamide	Acme
Advacide PMA	Phenylmercuric acetate	Advance Division
Advacide PMO	Phenylmercuric oleate	Advance Division
Advacide 60	Phenylmercuric oleate	Advance Division
Agrosol	Methyl mercury dicyandiamide	Chipman
Agrox C	Ethyl mercury chloride and phenylmercuric acetate	Chipman
Agrox	Phenyl mercury urea	Chipman
Calo-clor	Mercuric chloride, mercurous chloride	Mallinckrodt
Calo-gran	Mercuric chloride, mercurous chloride	Mallinckrodt
Calocure	Mercury	Mallinckrodt
Calogreen	Mercury (calomel)	Mallinckrodt
Centerchem	Mercuric chloride	Center Chemical, Incorporated
Ceresan L	Methyl mercuric acetate Methyl mercury 2,3-dihydroxy propylmercaptide	Du Pont
Ceresan M	Ethylmercuric p-toluene sulfonanilide	Du Pont
Ceresan M-DB	Ethylmercuric p-toluene sulfonanilide	Du Pont
"Ceresan" Red	Ethylmercuric chloride	Du Pont
Chipcote 25	Methyl mercury nitrile	Chipman
Chipcote 75	Methyl mercury nitrile	Chipman
Coromerc C	Phenyl mercury	Davison
Coromerc Liquid	Phenyl mercury	Davison
Doggett Fison Dap Cal	Mercuric chloride, mercurous chloride	Doggett Fiser
Doggett Fison Dap Cal	Phenylmercuric acetate	Doggett Fiser
Doggett Fison Turf Tox MC	Mercuric chloride, mercurous chloride	Doggett Fiser
Emmi	N-Ethylmercuri-1,2,3,6,-tetrahydro-3,6-endo-methanol-3,4,5-677 hexachlorphthalimide	Velsicol
E-Z Flo Puratized	Phenylmercuric monoethanolammonium lactate	E. Z. Flo
Fung Chex	Mercuric chloride, mercurous chloride	Wood Ridge
Gallotox	Phenylmercuric acetate	Guard
Gallotox 51	Volatile mercury compounds	Guard
Green Cross Erad	Phenylmercuric acetate	Green Cross
Green Cross Liquid Merlane	Methyl mercury-8-hydroxyquinolinate	Green Cross
Green Cross Liquid San	Methylmercuric acetate Methyl mercury 2,3-dihydroxy propylmercaptide	Green Cross
Green Cross Merlane Dust	Methyl mercury pentachlorophenolate	Green Cross
Green Cross San Dust	Methyl mercury pentachlorophenolate	Green Cross
GSCI	Mercurous chloride	Gallard-Schlesinger
GSCI	Mercuric chloride	Gallard-Schlesinger
Kroma-Clor	Mercury dimethyl dithiocarbamate	Mallinckrodt
Liquiphene Apple Scab Fungicide	Phenylmercuric acetate	Vineland
Liquiphene Turf Fungicide	Phenylmercuric acetate	Vineland
Mema	Methoxyethyl mercury acetate	Chipman
Memmi	N-methylmercuri-1,2,3,6-tetrahydro 3,6-endomethano-3,4,5,6,7,7-hexachlorophthalimide	Velsicol
Merbam	Phenylmercuric dimethyldithiocarbamate	Chipman
Mercuram	Phenylmercuric dimethyldithiocarbamate	Vineland
Mergamma	Phenyl mercury urea	Chipman
Mergamma C	Ethylmercuric chloride and phenylmercuric acetate	Chipman
Mergamma Liquid	Methyl mercury dicyandiamide	Chipman
Mersolite 88	Phenylmercuric acetate	Wood Ridge
Mersolite 88 W	Phenylmercuric acetate	Wood Ridge
Mersolite 810	Phenylmercuric acetate	Wood Ridge

TABLE A-4. (Continued)

Commercial or Trade Name	Active Mercury Ingredient	Manufacturer/Distributor/ Formulator
Mersolite 830	Phenylmercuric acetate	Wood Ridge
Metasol 10	Phenylmercuric acetate	Metal Salts
Metasol Bi-Cal	Mercuric chloride, mercurous chloride	Metal Salts
Metasol EMCL	Ethylmercuric chloride	Metal Salts
Metasol MMH Concentrate	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol MMH Dual purpose	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol MMH Liquid-dual purpose	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol MMH Liquid seed treatment	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol MMH mercury drill box formulation	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol MMH powder	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol MMH regular	Methyl mercury-8-hydroxy quinolinate	Metal Salts
Metasol Thiram Mercury	Mercuric chloride and mercurous chloride	Metal Salts
Miller (Puratized) Apple Spray	Phenylmercuri monoethanolammonium acetate	Miller Chemical & Fertilizer
Millers Puraspra	Phenylmercuric triethanolammonium lactate	Miller Products
Morsodren	Methylmercury dicyandiamide	Morton
NS DS	Phenylmercuric triethanolammonium lactate	Guard
New York Science Supply	Mercuric chloride	New York Science Supply
Niagara Puratized agricultural spray	Phenylmercuric triethanolammonium lactate	Niagara
Nuodex PMA-18	Phenylmercuric acetate	Nuodex
Nuodex PMO-10	Phenylmercuric oleate	Nuodex
Ortho-LM Apple Spray	Methylmercury-8-hydroxyquinolinate	Chevron
Ortho-LM Seed Protectant	Methylmercury-8-hydroxyquinolinate	Chevron
Panogen 15	Methylmercury dicyandiamide	Morton
Panogen 42	Methylmercury dicyandiamide	Morton
Panterra	Methylmercury dicyandiamide	Morton
Parson's Ready Mix seed treatment	Chloromethoxypropyl mercuric acetate	Parsons
Parson's Slurry Concentrate	Chloromethoxypropyl mercuric acetate	Parsons
Pearson's Merc-O-Dust	Mercurypentanedion	Pearsons
Phelam	Phenylmercuric dimethyldithiocarbamate	Wood Ridge
Phenmad	Phenylmercuric acetate	Mallinckrodt
Phenyl mercury fungicide	Phenylmercuric acetate	Agway
PM 2,4-D	Phenylmercuric acetate	Cleary
PM ACETATE	Phenylmercuric acetate	Guard
PMAS	Phenylmercuric acetate	Cleary
PMB	Phenylmercuric borate	Guard
Proturf fertilizer and fungicide	Phenylmercuric acetate	Scott
Proturf fungicide	Phenylmercuric acetate	Scott
Purasan PMA	Phenylmercuric acetate	Guard
Puraseed	Mercury compound	Guard
Puratized Apple Spray	Phenylmercuric monoethanol Ammonium acetate	Metasol Canada, Limited
Puratid	Phenyl mercury	Guard
Puraturf No. 10	Phenylmercuric acetate	Metasol Canada, Limited
Puraturf 10	Phenylmercuric monoethanolammonium lactate	Guard
Quicksan	Phenylmercuric acetate	Stecker
Quicksan 20	Phenylmercuric acetate	Stecker
Quicksan C20	Chloromethoxypropylmercuric acetate	Stecker
Quicksan CMA	Chloromethoxypropylmercuric acetate	Stecker
Real-Kill Moth Proofer	Phenylmercuric lactate	Cook Chemical Company
Samin Corp	Ethylmercuric chloride	Samin Corporation
Samin Corp., Mercuric Chloride	Mercuric chloride	Samin Corporation

TABLE A-4. (Continued)

Commercial or Trade Name	Active Mercury Ingredient	Manufacturer/Distributor/ Formulator
Samin Corp. Mercury Oxide	Mercuric oxide	Samin Corporation
Scutl	Phenylmercuric acetate	Scott
Semesan Bel	Hydroxymercurichlorophenol	Du Pont
Semesan Seed Disinfectant	Hydroxymercurichlorophenol	Du Pont
Semesan Turf Fungicide	Hydroxymercurichlorophenol	Du Pont
Setrete	Phenylmercuric ammonium acetate	Cleary
Setrete-Fortified	Ethylmercuric acetate and phenylmercuric acetate	Cleary
Setrete Mist	Ethylmercuric acetate and phenylmercuric acetate	Cleary
Shepard Chemical EMA	Ethylmercuric acetate	Shepard
Shepard Chemical EMC	Ethylmercuric chloride	Shepard
Shepard Chemical EMP	Ethylmercuric phosphate	Shepard
Stauffer Mer-CAD	Phenylmercuric formamide	Stauffer
Stauffer Mer-Sol 7	Phenylmercuric ammonium acetate	Stauffer
Stauffer Mer-Sol 48	Phenylmercuric acetate and ethylmercuric acetate	Stauffer
Stauffer Mer-Sol 51	Phenylmercuric acetate and ethylmercuric acetate	Stauffer
Tersan OM	Hydroxymercurichlorophenol	Du Pont
Troysan CMP Acetate	Chloromethoxypropylmercuric acetate	Troy
Troysan PMA	Phenylmercuric acetate	Troy
Troysan PMB	Phenylmercuric borate	Troy
Troysan PMO	Phenylmercuric oleate	Troy
Ultraclor	Mercuric dimethyldithiocarbamate	Mallinckrodt
Wood Ridge Calomel	Mercurous chloride	Wood Ridge
Wood Ridge Corrosive Sublimate	Mercuric chloride	Wood Ridge
Wood Ridge Mixture 21	Mercuric chloride and mercurous chloride	Wood Ridge

TABLE A-5. TYPES OF MERCURIALS USED IN DIURETICS

Name	Active Mercury Ingredient	Manufacturer
Chlormerodrin	[3-(Chloromercuri)-2-methyloxy]propylurea	Lakeside
Cumertilin	Same as Mercumatilin	Endo
Dicurin	Same as Merethoxylline procaine	Lilly
Diucardyn	Same as mercaptomerin	Ayerst
Diumerin	Same as mercurophylline	C. D. Smith
Diursal	Sodium (ortho[γ-hydroxymercuri-β methoxypropylcarbamyl] phenoxy) acetate	Various manufacturers
Mercuhydrin sodium	Same as Sodium meralluride	Lakeside
Mercumatilin	8-(2'-Methoxy-3'-hydroxy-mercuripropyl)-coumarin-3-carboxylic acid	Endo
Mercurophylline sodium	Sodium[(β-methoxy-γ-hydroxy-mercuri-propyl]-α-camphoramate	Various manufacturers
Mercupurin	Same as Mercurophylline	Various manufacturers
Mercuzanthin	Same as Mercurophylline	Campbell
Merethoxylline procaine	Dehydro-2-[N-(3'-hydroxymercuri-2'-methoxethoxy) propylcarbamyl]phenoxyacetic acid	Lilly
Mersaline	Same as Mersalyl	Various manufacturers
Mersalyl	Sodium salt of o-[(3-hydroxymercuri-2-methoxypropyl) carbamyl]phenoxyacetic acid	Various manufacturers
Mersalyl and Theophylline	Same as Mersalyl	Massengill
Mersalyn, Amp	Same as Mersalyl	Kirk
Neohydrin	Same as Chlormerodrin	Lakeside
Neomersyl, Amp	Same as Diursal or Mersalyl	Central
Salyrgan	Same as Mersalyl	Winthrop
Salyrgan and Theophylline	Same as Mersalyl	Winthrop
Sodium meralluride	Sodium 1-(3'-hydroxymercuri-2'-methoxypropyl)-3-succinylurea	Lakeside
Sodium mercaptomerin	Disodium N-3-(carboxymethylthiomercuri)-2-methoxypropyl]-α-camphoramate	Wyeth
Thiomerin sodium	Same as Sodium mercaptomerin	Wyeth

TABLE A-6. USE OF MERCURIALS IN ANTIINFECTIVES (ANTISEPTICS)

Name	Active Mercury Ingredient	Manufacturer
Meralein sodium	Monosodium salt of 2,7,diiodo-4-hydroxymercuri-resorcinsulfonphthalein	Hynson, Wescott, and Dunning
Meralluride	Methoxyhydroxymercuripropylsuccinylurea	Lakeside
Merbromin (Mercurochrome)	Dibromohydroxymercuri fluorescein	Hynson, Wescott, and Dunning
Mercarbolide	o-Hydroxyphenylmercuric chloride	Upjohn
Mercresin	p-Hydroxyphenylmercuric chloride	Upjohn
Mercresol	Same as Mercresin	Upjohn
Mercurophen	Sodium hydroxymercuri-o-nitrophenolate	Merck, Sharpe, and Dohme
Merodicein	Same as Meralein	Hynson, Wescott, and Dunning
Merthiolate	Same as Thimerosal	Lilly
Metaphen	Anhydride of 4-nitro-3-hydroxymercuri-o-cresol	Abbott
Nitromersol	Same as Metaphen	Abbott
Thimerosal	Ethylmercurithiosalicylate	Lilly

Trade Name	Manufacturer
Phenylmercuric Acetate	
Contra Creme	Contra
Monaserts	Wintersmith
Triserts	Ulmer
Kenhex	Kendall
Trinalis	Webster
Di-Spor Ointment	Wintersmith
Aquacort	Webster
Vagitabs	Ascher
Clasol	Vitamix
Phenylmercuric Borate	
Dermathyn Ointment	Davis and Sly
Mertricone	William H. Rorer, Incorporated
Phenylmercuric Lactate	
Gluco-Thricil	Parke, Davis & Company
Phenylmercuric Nitrate	
Merphene	Barry Laboratories, Incorporated
Merphenyl nitrate	Hamilton
Phe-Mernite	Massengill
Phenalco	Chicago Pharmacal Company
Phenitol (solution and ointment)	Chicago Pharmacal Company
Phenmerzyl nitrate	Pitman-Moore
Merlenate (ointment and powder)	Chicago Pharmacal Company
Phenylmercuric Oleate	
Mercene	Matbie
Phenylmercuric Picrate	
Merphenyl Picrate	Hamilton.

Only small quantities of inorganic mercury compounds – for example, mercuric chloride; mercuric iodide; red mercuric oxide; yellow mercurous chloride; mercurous iodide; yellow, ammoniated mercury; and mercuric chloride – are now being used. This market probably will continue to dwindle in favor of organic mercurials or less toxic materials.

Manufacturers of mercury chemicals consumed in the production of diuretics and antiseptics are:

Allied Chemical Corporation, General Chemical Division
American Firstoline
Atomergic Chemical Metals
J. T. Baker Chemicals
W. A. Cleary Corporation
Electronics Space Products
D. F. Goldsmith, Chemical and Metal
H. Kohnstamm and Company
Mallinckrodt Chemical Works
McKesson and Robbins
Metasol Products
Robeco Chemicals

Rocky Mountain Research	Troy Chemicals
Steritized, Incorporated	Wood Ridge Chemicals

Dental Preparations.(A-30) Mercury consumption in dental preparations during 1965 showed a 38 percent decline over 1964. Future use probably will level off or show a still further decline. Other metals, base-metal alloys, porcelain, and especially plastics - e.g., acrylics, vinyl-acrylic copolymers, polystyrenes, and epoxy systems - are strongly competitive materials. Acrylics and copolymers of acrylics dominate the field. The versatility of the acrylics has expanded their range of dental applications to include full denture bases, partial dentures, bridgework, jacket crowns, inlays, orthodontic splints, artificial teeth, tooth-restorative materials, repair materials, impression trays, patterns for cast metallic inlays, and denture liners. Technology rather than cost seems to be the reason for the replacement of mercury by suitable plastics. The cost of mercury is a minor item because of the quantities used and because of the proportionately high labor cost.

Catalysts.(A-31 - A-34) Mercury consumption in this category in 1965 showed a 29 percent increase over 1964. The most important use of mercury as a catalyst has been in the hydration of acetylene to make acetaldehyde. The manufacture of vinyl acetate and vinyl esters of fatty acids frequently involves the use of mercury catalysts. However, industrially, both processes are becoming less significant. Large quantities of acetaldehyde now are manufactured by:

(1) Dehydrogenation of ethyl alcohol
(2) Air oxidation of ethyl alcohol.

These processes do not employ mercury catalysts. With varying degrees of success, considerable effort has been directed toward the manufacture of nonmercurial catalysts for the manufacture of vinyl acetate. However, the main determinant of acetylene consumption in vinyl acetate by 1970 will be the comparative economics of the new ethylene-based route versus the traditional acetylene-acetic acid route. Until this matter is resolved, it is expected that the existing vinyl acetate plants utilizing acetylene will be incrementally expanded to take advantage of low-capital expansion opportunities. In this case, even without new plants, it is possible that the 1970 capacity of vinyl acetate based on acetylene will approximate 600 million lb/year. Much of this vinyl acetate manufacture would be expected to involve the use of mercury catalysts. Table A-7 is a list of the United States producers of vinyl acetate monomers.

Vinyl chloride ($CH_2=CHCl$) monomer is produced by two routes:

(1) Reaction of HCl with acetylene in the presence of a catalyst such as mercuric chloride. One pound of mercuric chloride produces about 1,000 lb of vinyl chloride.

(2) Oxychlorination of ethylene to make ethylene chloride, which is subsequently cracked to vinyl chloride.

Current vinyl chloride production capacity and planned expansions are given in Table A-8.

TABLE A-7. UNITED STATES PRODUCERS OF VINYL ACETATE MONOMERS

Company	Location	Raw Material	Capacity, millions of lb/yr
Air Reduction	Calvert City, Kentucky	Acetylene-acetic acid	90
Borden	Geismar, Louisiana	Acetylene-acetic acid	75
Celanese	Bay City, Texas	Ethylene-acetic acid	100
	Pampa, Texas[a]	Acetaldehyde-acetic anhydride	65
Du Pont	Niagara Falls, New York	Acetylene-acetic acid	90
Monsanto	Texas City, Texas	Acetylene-acetic acid	55
National Starch	Long Mott, Texas	Acetylene-acetic acid	50
Union Carbide	South Charleston, West Virginia	Acetylene-acetic acid	50
	Texas City, Texas	Acetylene-acetic acid	110
Total U. S. capacity			685
Amount based on acetylene route			520

(a) Industry reports indicate Celanese either has closed this plant or is planning to do so.

Table A-8 lists the present capacities of United States producers of vinyl chloride and additions planned by four companies.

Sulfonation products of anthraquinone are important starting materials for the manufacture of vat dyes. They are usually marketed as 1-anthraquinone sulfonic acid sodium salt (more than 5 million pounds per year produced in the United States), as 2-anthraquinone-sulfonic acid, or as 1, 5-dihydroxyanthraquinone (obtained from the corresponding disulfonic acids). With the exception of the 2-anthraquinone sulfonic acid, all mono- and disulfonic acids of anthraquinone require use of a mercury-salt catalyst for sulfonation.

Mercury catalysts have been tried as esterification, hydration, reduction, oxidation, dehydrogenation, chlorination, fluoridation, sulfurization, sulfonation, isomerization, polymerization, and disproportionation catalysts. Only in the manufacture of acetaldehyde vinyl acetate, vinyl chloride, and sulfonated anthraquinone have they reached industrial significance. However, there are several areas in which current research might make mercury catalysts attractive in additional industries. These areas include:

- Preparation of fluorochemicals
- Ziegler-type reactions
- Curing of polymers (as a cross-linking catalyst)
- Photochemical reactions
- Additional sulfonation reactions, e.g., preparation of dyes and dye intermediates.

The important mercury compounds that are used industrially or experimentally as catalysts are:

Mercury	Mercuric oxide
Mercuric acetate	Mercuric phosphate
Mercuric chloride	Mercuric sulfate.

TABLE A-8. PRESENT AND PLANNED EXPANSION OF VINYL CHLORIDE PRODUCTION CAPACITY(A-31)

Company	Capacity, millions of pounds	Process
	Present Producers	
Allied	100	Acetylene
American Chemical (Richfield-Stauffer)	170	Ethylene oxychlorination
Cumberland Chemical (Air Reduction)	60	Acetylene
Diamond Alkali	100	Acetylene
Dow	400[a]	Ethylene oxychlorination
Ethyl	420[a]	Ethylene oxychlorination
General Tire	75	Acetylene
Goodrich	440[a]	Ethylene oxychlorination; acetylene (40)
Goodyear	70	Acetylene
Monochem (Borden-U. S. Rubber)	250	Acetylene
Monsanto	150	Acetylene and ethylene oxychlorination
Tenneco	200	Acetylene
Union Carbide	335[a]	Balanced process
Total	2,770	

Company	Description
	Planned Additions
Dow	Adding 600-650 million lb by an expansion at Freeport, Texas, and a new plant at Placquemine, Louisiana. Scheduled for early 1968.
PPG	First half of 300-million-lb/yr plant due in fall of 1967 at Lake Charles, Louisiana.
Stauffer-Conoco	Construction will start this year on 500-million-lb/yr plant at Lake Charles, Louisiana.
Allied	Groundbreaking expected this year for a $30-million plant (estimated at 500-600 million lb/yr) at Baton Rouge, Louisiana.

(a) Plants at two locations.

Amalgamation. During 1965, the use of mercury in alloys was 495 flasks, or about a 26 percent decrease over 1963. For economic reasons, and because of technological advances, this market probably will not be recaptured.

Almost all metals can be amalgamated with mercury, the prominent exception being iron. Depending upon the metal and the amount being alloyed, the resulting mixture is either liquid or solid.

Mercury was widely used in the early days of gold mining to recover free gold and silver from placer and lode ores. Use practically disappeared when the free-milling ores were depleted and when the cyanide process was developed. The alloying properties of mercury are its valuable function in dental applications.

Potassium, sodium, and zinc amalgams are used as reducing agents. Zinc amalgam is used in the reduction of γ-keto acids. Sodium amalgam has been used in production of tetraethyl lead. However, a continuous electrolytic process suitable for producing either tetraethyl lead or tetramethyl lead threatens to curtail further the use of sodium amalgam. The alloying characteristic is used in conjunction with mercury's electrical conductivity to make mercury valuable in electrolysis cells. The pronounced success of mercury as an electrode in chlorine cells encouraged its use for similar purposes, particularly where a metal is released that will amalgamate sufficiently. Uranium and vanadium can be separated and recovered by such electrolysis of carbonate-leach solutions. Whether or not usable fuel can be so reclaimed from reactor cores is not known. However, as nuclear reactors become more numerous, reclamation of fuel by amalgamation may become significant.

An electrolytic process for recovery of zinc from drosses or other by-products involves precipitation of zinc elements at the cathode and alloying with mercury. The mercury forms a moving cathode, and as it is extracted from the electrolytic cell it carries a small amount of zinc. The zinc is then deposited on an aluminum cathode and can be stripped electrolytically. Zinc of high purity is recovered.

Amalgam metallurgy also has been tried for the recovery of aluminum, bismuth, cadmium, copper, indium, lead, manganese, nickel, sodium, tin, and thallium. None of these operations has proven economically attractive. Generally, amalgamation seems to be a dwindling market for mercury.

Paper and Pulp Manufacture.(A-35 – A-38) Mercury consumption in the manufacture of paper and pulp showed a drastic drop from 2,148 flasks in 1964 to 619 flasks in 1965, a 71 percent decline. This sharp drop is attributed to:

(1) The toxicity of mercury compounds to human and marine life
(2) The subsequent use of more effective and cheaper substitutes.

At first it was believed that the concentrations at which organic mercurials were used in pulp and paper industries were so low as to render them comparatively innocuous. This is not necessarily true, since paper derived from pulps treated with organic mercurials as a slimicide may contain sufficient mercury to be toxic to some individuals. Indeed, it is inadvisable to use paper processed with organic mercurials as food wrappers. The toxicity of small concentrations of organic mercurials to salmon and trout has been substantiated. Consequently, the use of organic mercurials in pulp and paper processes is rapidly decreasing in favor of such substitutes as chlorine, chlorine dioxide, copper sulfate, salts of polychlorophenates, ozone, zinc salts, quaternary ammonium salts, polyamines, alkyl and aryl dithiocarbamates, and bis(tri n-butyl tin)oxide.

Organic mercurials that have been used in pulp and paper processes include:

Phenylmercuric acetate
Phenylmercuric borate
Phenylmercuric bromide
Phenylmercuric lactate
Pyridylmercuric acetate
bis(Phenyl mercuric) ammonium propionate
poly(Oxyethylene) phenylmercuric acetate

Manufacturers and distributors of slimicides and slime-control agents, including organic mercurials for pulp and paper processes include:

Aldrich Chemical Corporation
Buckman Laboratories
Calgon Corporation
Dow Chemical Company
Drew Chemicals
Eastman Organic Chemicals
Fine Organics
Fleetwood Chemical Company, Incorporated
Givaudan Corporation
General Aniline and Film, Dyestuff and Chemical Division
Houghton and Company, E. F.
Ionac Chemicals
Magnus Chemical Company
M& T Chemicals
Metasol Products
Monsanto
Nalco Chem
Oakite Products
Olin Mathieson Chemical Corporation
Sandoz, Incorporated
Stecker Chemicals
Steritized, Incorporated
Tennessee Corporation, Industrial Chemicals
Utility Chemical Company
Vanderbilt Company, Incorporated
Vineland Chemicals
Wood Ridge Chemicals
Wyandotte Chemicals

Recent Research

Research in 1965 and 1966 led to the following developments in mercury:

- New advances in mercury lamps, which promise modifications of some current systems

- The description of an automatic vacuum mercury still that is useful in distilling mercury for use in McLeod gages, diffusion pumps, polarographic and other equipment

- The publication of a review of mercury marketing, together with a discussion of mercury economics

- The publication of detailed discussions of various types of mercury cells for producing chlorine and caustic soda, together with cost data, trends, advantages, and disadvantages.

- A review of antimicrobial agents for plastics includes the evaluation of organic mercurials

- The use of phenylmercuric acid for reducing stomatal apertures to decrease transpiration rate (20 percent for grasses and almost 50 percent for lettuces).

Toxicity Information

There is an extensive literature on the toxicology of mercury. Comprehensive reviews of this literature are found in Bidstrup(A-41), King(A-59), Browning(A-43), Stokinger(A-71), Battigelli(A-40), Goodman and Gilman(A-57), and the series of articles from the Columbia group, Goldwater, Jacobs, and Ladd (see Bibliography). Research in the toxicology of mercury is widely scattered; however, there are at least four prominently active research groups: Columbia University (Goldwater, et al.); University of Rochester (Clarkson, Rothstein, Hodge, et al.); the British group (Magos, et al.); and the Swedish group (Berlin, et al.). There is also a considerable amount of important research from Russia and Japan, the latter primarily concerned with mercury contamination of food fish in Minamata Bay by industrial wastes.

Mercury has been known to be toxic since prehistoric times. King(A-59) states that there are indications that it was known in the 15th and 16th Centuries B. C. Hippocrates, in about 400 B. C., as well as the Indians and Persians, described uses of mercury as drugs. Antidotes for mercury poisoning appeared as early as 1241 A. D. Ulrich Ellenbog in 1524 and Jean Fernel in 1557(A-51) described at length the dangerous effects of mercury vapor.

Incidence of Mercury Poisoning

Prior to the enforcement of hygienic practices in industry, industrial exposures to mercury were the chief sources of poisoning. Nonindustrial deaths due to accidental poisoning in the United States for the years 1955 to 1964 have been cited by Press(A-69). These ranged from 3 to 11 per year. There are several reports of mercury poisoning in laboratories in which evaporation from uncovered vessels or from spilled droplets has played a role(A-51). Poisoning from dental amalgam has been less a problem with improved technology in dental practice but still is reported in other countries.(A-61) Hoover and Goldwater(A-58) have recently reviewed dental-amalgam usage and have shown by their study that amalgams in this country do not appear to be an important source of mercury absorption.

In the United States, the first mention of mercury as an industrial hazard appeared in about the middle of the 19th century in connection with employing mercurial "carrot" (mercury nitrate). At one time at least 80 industries were listed as using mercury. Battagelli(A-40) discussed briefly some of the more important sources of industrial mercury poisoning. These were mining and refining, the felt-hat industry, technical instruments, and manufacture of carbon brushes for fluorescent lights. Battigelli compiled a review of case histories as shown in Table A-9. Gefafer(A-49) provides a list of current potential occupational exposures, shown in Table A-10. Recent industrial exposure in Philippine mines have been cited by Ladd(A-65) and by Broadhurst(A-42), who compiled 41 case histories for the years 1956 to 1964 in several British factories.

TABLE A-9. MERCURY POISONING BY INHALATION: HUMAN CASE EXPERIENCE IN VARIOUS INDUSTRIES(A-40)

Author and Year	Industry	Compound or Material	Air Concentration, mg/m^3 air	Length of Exposure	Mercurialism Incidence in Exposed Workers
Neal et al. (1937)	Fur cutting	$HgNO_3$; (Hg)	<0.2	2 or more years	4.5% affected
Neal et al. (1937)	Fur cutting	$HgNO_3$; (Hg)	<0.2	2 or more years	17.1% affected
Neal et al. (1941)	Felt-hat manufacture	$HgNO_3$; (Hg)	0.16-0.23	10-19 years	17.5% affected
Bidstrup et al.	D-c meter repair	Hg elemental	0.22-1.6	Months	26% affected
Bell et al.(a)	Laboratory	Hg elemental	0.15	7 months	Single case
Goldwater et al. (1956)	Laboratory	Hg elemental	0.1-0.2	1 year	Single case
Kesic et al. (1951)	Mining and smelting	Hg elemental	0.25-5.9	Years	31.6% affected
Kesic et al. (1951)	Felt-hat manufacture	$HgNO_3$	0.25-1.0	Years	67.7% affected (women)
Benning (1958)	Carbon-brush manufacture	Hg elemental	0.2-0.75	Months	69% affected
Hill (1943)	Fungicides	Diethyl Hg	1.0	3 months	2 deaths
Dinman et al. (1958)	Chemical industry	Organic Hg derivatives	2.9-16.9	Acute episodic exposure	3 acute cases
Massmann (1957)	Chemical industry	Phenyl mercury pyrocatechol	0.24-3.20	Months	No intoxication
Dinman et al. (1958)	Chemical industry	Organic Hg derivatives	0.01-0.1	Years	No intoxication

(a) Case resulted from exposure to Hg vapor at low atmospheric pressure.

TABLE A-10. POTENTIAL OCCUPATIONAL EXPOSURES(A-49)

- Amalgam makers
- Bactericide makers
- Barometer makers
- Battery makers, mercury
- Boiler makers
- Bronzers
- Calibration-instrument makers
- Cap loaders, percussion
- Carbon-brush makers
- Caustic-soda makers
- Ceramic workers
- Chlorine makers
- Dental-amalgam makers
- Dentists
- Direct-current-meter workers
- Disinfectant makers
- Disinfectors
- Drug makers
- Dye makers
- Electric-apparatus makers

Pharmacology

Mercury is unique among the heavy metals in that it has considerable volatility at ordinary room temperatures. At 25 C, the equilibrium concentration is about 20 mg/m^3, or about 200 times the threshold limit value of 0.1 mg/m^3 recommended as the maximum atmospheric concentration for a normal work schedule by the American Conference of Governmental Hygienists.

Mercury readily forms covalent linkages to sulfur, and it is this property that accounts for most of its biological activity. When the sulfur is in the form of sulfhydryl groups, divalent mercury replaces the hydrogen atom to form mercaptides X-Hg-SR and $Hg(SR)_2$, where X is an electronegative radial and R is protein. Organic mercurials form mercaptides of the type $R\text{-}H_g\text{-}SR$. The pharmacological effects of mercury vary widely according to the nature of the chemical compound administered.

The covalent bonding of mercury in many of its compound forms allows elemental mercury to evaporate from the compound. The volatility of mercury and its compounds has been emphasized by Kelly et al., by Burgh et al.(A-70), and the Hg^{203} method of assay for mercury in biological samples(A-45). This volatility was shown to occur by Clarkson when he demonstrated the ability of mercuric ion bound to hemoglobin to convert to mercury vapor.(A-45) Other studies by Clarkson showed that the body, whole blood, and tissue homogenates also were able to give off mercury. Clarkson also showed that a microorganism, *Klebsiella aerogenes*, increased this volatilization from urine. Thus, one needs to be aware of the possible mobility of mercury relative to its chemical form and its environment (biological and otherwise).

Determination of Mercury. Several methods are used for the determination of mercury(A-90, A-41, A-53). For biological materials a dithizone is frequently used. Jacobs et al. have developed a method for the estimation of mercury in blood, urine, kidney tissue, fruits, vegetables, water, and fabrics that was modified so that only 0.1 ml blood or other material is required.(A-64) The method involves digestion of organic matter in the cold to inhibit loss of mercury from the sample by volatilization, extraction of the mercury by dithizone, decomposition of the dithizonate by heating, and estimation of the mercury vapor by ultraviolet photometry. Either a photometer or a selenium sulfide paper can be used to detect mercury in air. A sensitive, newer method using exchange reactions of Hg^{203} is finding increased use to detect mercury in both air and biological materials.(A-67)

Mechanism of Action. Although the biological effects of mercury vary according to the form in which it is absorbed and the rate of absorption, the principal reaction of mercury from whatever source is with thiols, forming mercury mercaptide. Since sulfhydryl groups occur frequently in body proteins and have varying affinities for mercury, the exact sites of pharmacological activity are not known. There is evidence that mercury also specifically inhibits enzyme systems *in vitro*.

Absorption, Distribution, and Excretion.(A-57) The absorption, distribution, and excretion of mercury and its compounds varies considerably with the chemical form of the metal. It is generally considered that *mercury metal* is not absorbed from the intestinal tract, but that mild catharsis, diuresis, or intoxication from the ingestion of the metal results from films of oxides or sulfides formed on the surface of mercury that has been exposed to the atmosphere. In water, especially in the presence of chloride ion, mercury can be slowly oxidized by atmospheric oxygen to the mercurous form which, in turn, can be further oxidized to yield mercuric ions. So long as the state of subdivision of the mercury is quite coarse, the rate of solution in body fluids is too slow to give rise to cumulative effects. However, inhaled mercury vapor can oxidize rapidly enough to induce a state of intoxication if the exposure is sufficient. Also, elemental mercury absorbed by the lungs gradually concentrates in nervous tissue. The fact that elemental mercury can be absorbed through the skin may derive from its lipid solubility.

The soluble inorganic mercurials readily gain access to the circulation when taken by mouth, although a considerable portion of the ingested mercury may remain fixed to the alimentary mucosa and the intestinal contents. Insoluble inorganic mercurous compounds, such as calomel (Hg_2Cl_2), may undergo some oxidation to soluble, absorbable compounds. In suitable vehicles, inorganic mercurials may be absorbed through the intact skin. Excretion of mercury starts immediately after absorption, mainly by way of the kidney and colon, and to a lesser extent, via the bile and saliva. Tissue concentrations fall at different rates, so that the distribution changes slightly over the course of time. The mercury content of the brain falls especially slowly. Most of the mercury is excreted within 6 days after administration, but traces may be detected for months. The urinary excretion of mercury may be hastened by dimercaprol.

The absorption, distribution, and excretion of the organic mercurials vary widely among the types of compounds. In animals, phenylmercuric compounds appear to be converted in the body to inorganic compounds, and thus ultimately show a distribution similar to that of inorganic mercury. However, the mercury of phenylmercuric acetate is excreted more rapidly than that of mercuric acetate. The mercurial diuretics meralluride and mersalyl do not appear to release significant amounts of inorganic mercury in the body, and may be excreted largely intact in combination with thiols. Although they are said to penetrate the tissues poorly, and thus to reach high concentrations only in the kidney, the occurrence of nonrenal toxic effects reveals that significant amounts of mercury may reach all of the body tissues. Excretion is much slower than for other mercurials, even though the concentration in blood may be quite high. The brain contains a higher content of methylmercury relative to the total body burden than it does when other mercurials are given.

Mercury in Tissues.(A-40) The amount of mercury that can be absorbed without giving rise to symptoms is not known. Available evidence suggests that it varies for different individuals, and the rate of absorption obviously plays an important part. Localization in particular tissues does not necessarily give rise to pathological changes.

Griffith et al. in 1954 [see Reference (A-41)] reported mercury present in the tissues in all cases in 910 autopsies. He studied 45 cases particularly in which death was due to congestive cardiac failure. In 15 to whom mercurial diuretics had not been administered during life, the average concentrations of mercury, in mg/100 g dry tissue, were, for the kidney, 2.05; the liver, 0.37; and the spleen, 0.12; in 14 who had received 400 mg or less of mercury, the kidney concentration was 2.96, and in 16 who had received more than 400 mg mercury, and an average 4,692 mg during life, the average concentrations were 15.29 in the kidney; 1.38 in the liver; and 0.32 in the spleen. They concluded that mercury was present in the tissues of persons who were not known to have occupational or therapeutic exposure to it during life; that the therapeutic administration of organic mercurial diuretics increased the concentration of mercury in the tissues, particularly in the kidney; but that no pathological changes resulted that could be ascribed to the accumulation of mercury in these cases. Leff and Nussbaum [see Reference (A-41)] in 1957 reported that less than 16 mg mercury/100 g dry tissue was present in the kidneys of a woman who died of congestive heart failure and who had been given 22,600 mg of mercury as mercurial diuretics during the last 5 years of her life. There was no evidence of damage to the glomeruli, renal tubules, liver cells, or heart muscle that could be attributed to the effects of mercury.

In two cases of the nephrotic syndrome occurring in men exposed to mercury in their occupations, biopsy specimens were found to contain 2.5 g and 1 g of mercury/100 g fresh tissue, respectively, and sections showed an abundance of lipoids in the epithelium of the proximal convoluted tubules that contained eosinophilic debris and albuminous casts. The mercury content of other tissues in fatal cases of poisoning from different types of mercury compounds are recorded in Table A-11.

TABLE A-11. MERCURY CONTENT OF HUMAN TISSUES(A-41)

Mercury Compound Absorbed	Dose or Period of Exposure	Interval Between Last Exposure and Death	Mercury Content of Tissues, parts per million							Reference
			Kidney	Liver	Brain	Spleen	Lungs	Heart	Blood	
CH_3HgX	'Chronic'		30	19	5		3			Ahlmark
	5 yr	1 month	3	14	4-9	4	2		4[a]	Lundgren and Swensson
									Serum	
Mercaptomerin	40 mg	0.4 day	9	1.8	0.2	0.9	1.7	0.8	2.8	Aikawa and Fitz
	80 mg	1.5 days	12	5		6	8	1.4	5.4	
	80 mg	2 days	17	1.8		0.6	1.3		0.9	
	80 mg	6 days	5	0.6	0	0.3	0.2	0.1	0.3	
Mercuric salts										
$Hg(C_6H_5COO)_2$	Inunction	37 days	63	12	1.5	6	1	3.7	1.1[b]	Lomholt
$HgCl_2$	Acute poisoning	3 days	70	32	1.7	10	6	3		
		6 days	16	3	1.0	4	0.3	2.4		
$HgCl_2$	2.5 g	6 days	35	25					1	Sollmann and Schreiber
	5.5 g	9 days	33	26					1.2	
	1 g	8 days	24	10					0.1	
Metallic vapor	19 yr	6 months	21	28	9	1.5				Brigatti
	7 yr	12 months			6-7	0.6				
	8 months		26	9	0-0.9			2.3		

(a) Blood taken day before death.

(b) Median value obtained by Lomholt for similar inunction treatments.

Toxicology

Clinical Mercury Poisoning.(A-57) Mercury poisoning may be acute or chronic. Acute poisoning usually results from the oral ingestion of highly dissociated inorganic preparations, although it may also result from inhalation of vapors of elemental mercury or from organic mercurials. Chronic poisoning, as a rule, follows industrial exposure or medicinal use. The common offenders among organic mercurials are ethylmercury or methylmercury compounds, such as methylmercury dicyandiamide, and phenylmercury compounds, such as phenylmercuric acetate. They are employed as fungicides, and as such are also incorporated into some water-base paints, from which poisonings have occurred. The differences in the distribution and excretion among mercurial compounds and variations among individuals with respect to sensitivity and rate of excretion of mercury obscure correlations between the clinical signs of intoxications, the level of exposure, and the excretion of the metal. Browning has reviewed in some detail mercurial poisoning in man and animals relative to the type and quantity of mercury exposure.(A-43) The following sections, taken from Goodman and Gilman(A-57), summarize poisoning in man.

Acute Mercury Poisoning. Acute poisoning is commonly caused by mercuric chloride or mercuric cyanide, taken either with suicidal intent or by accident. When mercuric chloride is ingested, the earliest evidence of the toxic action may be an ashen-gray appearance of the mouth and pharynx, which is the result of the precipitation of the protoplasm of the mucous membranes. This condition is very painful. The mucous membrane of the stomach is similarly affected, and gastric pain and vomiting result. Vomiting is often the determining factor in the ultimate course of the poisoning. If the stomach is quickly and effectively emptied, the patient's chance for survival is much greater. A high concentration of the poison may reach the epithelium of the small intestine. The local effect on the bowel soon results in a severe, profuse, bloody diarrhea. Shreds of intestinal mucosa can be identified in the stool. The local intestinal reaction may be sufficiently severe to cause profound shock, and death may result in a few hours from circulatory collapse. If the poisoning occurs by inhalation of fumes of metallic mercury or organic mercurials, the syndrome is characterized by pneumonitis, lethargy or restlessness, fever, tachypnea, cough, chest pain, cyanosis, diarrhea, and vomiting.

The patient commonly recovers from the local symptoms, especially if vomiting has been extensive or chemical antidotes have been administered. The systemic effects of the poison start within a few hours and may last for days. Death may ensue. The systemic phase of poisoning by inorganic mercury and phenylmercuric compounds is characterized by the action of the mercuric ion diffusely on the capillary walls and specifically at the sites of excretion - the kidney, colon, and mouth. Mercury imparts to the saliva a strong metallic taste. Within 24 to 36 hours, a stomatitis develops, characterized by foul breath, soreness of gums, and excessive salivation. Discoloration of the gingival margins appears later, and local infection, loosening of the teeth, and necrosis of the alveolar processes may follow. Systemic signs of acute poisoning by elemental mercury and ethylmercuric or methylmercuric compounds include those referable to the central nervous system, such as lethargy, excitement, hyperreflexia, and tremor.

The toxic action of inorganic mercury on the kidney is usually the cause of death. The kidney may show evidence of disturbed function within a few minutes after the poison reaches the circulation. If the local action of the drug is not followed by profound shock and if the circulation is adequate, the first response of the kidney may be a diuresis. Soon, however, the renal damage becomes so extensive that oliguria and finally anuria result.

Chronic Mercury Poisoning. Chronic mercury poisoning results from exposure to small amounts of mercury over extended periods of time. The signs and symptoms characterizing this condition are gingivitis, stomatitis, loosening of the teeth, salivation, metallic taste, colitis, progressive renal damage, loss of appetite, nutritional disturbances, anemia, hypertension, and peripheral neuritis. The central nervous system is especially involved, as evidenced by behavioral changes, mental depression, irritability, insomnia, tremors and shaking, fatigue and drowsiness, and, occasionally, hallucinations. The ethylmercuric and methylmercuric compounds mainly cause neurological signs and symptoms, especially tremor, ataxia, dysarthria, constriction of the visual field, and, occasionally, psychosis.

Hypersensitivity. Hypersensitivity to mercury is uncommon but by no means rare. It is often unrecognized. Unusual responses to the mercurial diuretics occur. Reactions to inorganic preparations of mercury may give rise to bizarre clinical syndromes; they are usually encountered in persons treated with ointments. The response often takes the form of a cutaneous reaction. This may vary from a slight erythema, involving only the area of application, to a severe generalized eruption that may be morbilliform, punctate, or urticarial. Eventually, vesicles and bullae may appear. The skin reactions may be accompanied by fever and prostration. Cases have been reported in which individuals sensitive to mercury have experienced systemic reactions as a result of dental fillings with amalgam. Treatment consists in removal from contact with mercury, appropriate management of the skin lesions, and supportive measures. Metal-chelating agents are often without value.

Diagnosis of Mercury Poisoning. Acute mercury poisoning usually does not pose difficulty of diagnosis. Usually the source of the poison is identifiable and the signs and symptoms support the diagnosis. In case of suspected mercurial poisoning, recovery from mouth tissue scrapings, and blood and urine levels should establish the diagnosis. Persons without recognized exposure to mercury excrete less than 100 micrograms/24 hours in their urine and have a blood concentration less than 0.5 micrograms/100 ml.

Because of the insidious character and vague clinical picture of chronic mercurialism, the diagnosis would be more accurately formulated with the aid of laboratory data. However, no highly discriminating tests are available. In a comparison of mercury concentrations in biological fluids, the blood level of mercury seems to be the least reliable. The rapid loss of mercury from the blood stream after its absorption has been clearly demonstrated in experimental animals. Even though mercury levels in the blood of exposed persons are frequently found to be higher than levels in those not exposed, the variations among individuals and after various exposures precludes its practical use.

Therapy for Mercury Poisoning(A-40)

While acute intoxication is apparently helped by the dimercaprol (BAL) treatment, at the present time there is no satisfactory therapy for chronic mercurialism. In such cases, the use of dimercaprol has not only been of doubtful effectiveness, but it is even considered harmful by some investigators. Nevertheless, there are reports that favor its use in chronic intoxication. In this country, Bell, Gilliland, and Dunn [see Reference (A-40)] were able to increase significantly the urinary output of mercury by the administration of dimercaprol in a case of chronic intoxication. The chelating agent edathamil (ethylenediaminetetraacetic acid; EDTA), tried in the same case, did not produce any positive effect.

In cases of mild intoxication, the symptoms of mercurialism may regress significantly after exposure ceases. In a series of 135 cases reported by Baldi, Vigliani, and Zurlo [see Reference (A-40)] the great majority (79 percent) of the patients affected with slight mercurilaism showed a conspicuous improvement in 4 or 5 years after the exposure ceased. Patients with more advanced degrees of intoxication, however, are less likely to show improvement.

In the same clinical survey, only 15 percent of the patients with marked manifestations of mercurialism improved in the subsequent years. The outlook for those most seriously affected was even worse. One case described by Hunter may serve as a striking example. Fifteen years after an encephalopathic syndrome caused by a few months of exposure to methyl mercury compounds, the patient was still unable to resume any sort of work because of persistent ataxia, tremor, and astereognosis.

Lethal Dosages of Mercury

The quantities of mercury necessary to kill an individual depend on the compound, the amount and rate of exposure, and the species, in the case of animals. Fraser et al in 1934 reported the acute lethal concentration of mercury vapor for dogs as 15 to 20 mg/m^3; oral administration of $HgCl_2$ for dogs, 10 to 15 mg/kg; and 4 to 5 mg/kg for intravenous dosages.$^{(A-43)}$ Cat dosages were somewhat higher.$^{(A-68)}$ By inhalation, the lethal dose for mice of two organic mercury compounds – the ethyl phosphate and ethyl chloride – was given by Trakhtenberg in 1950 [see Reference (A-43)] as 0.01 to 0.04 and 0.03 to 0.044 mg/l, respectively. By intraperitoneal and intravenous injection, a number of organic compounds, which included methyl and ethyl mercury dicyanamide, methyl and ethyl chloride, phenylmercuric acetate and sublimate, have been extensively investigated by Lundegren and Swensson [see Reference (A-43)] These were all approximately 1 mg/100 g body weight. Intravenous injections of 16 mg/kg body weight of methyl mercury chloride and methyl mercury dicyanamide were sufficient to cause death.$^{(A-43)}$ LD_{50} values for mercurials are not easily available. Of some 90 compounds listed in the Merck Index, LD_{50} values were available for 4.

Dresibach [Reference (A-48), p 171) indicates that in man the fatal dose of mercuric salts is 1 g, and for a number of organic mercurials the dose is 3 to 5 times that of the soluble mercury salt. Browning [Reference (A-43), p 202] reported that corrosive sublimate by ingestion has caused the most frequent and severe symptoms, the fatal dose varying from 3 to 30 g.

Tolerance to Mercury

The amount of mercury that can be absorbed without giving rise to symptoms is not known. Available evidence suggests that it varies for different individuals and for different compounds (see Table A-9). The human organism is able to absorb and excrete considerable amounts of mercury without showing toxic manifestations. Measurable quantities are routinely ingested in the normal diet and humans "not exposed" to mercury show substantial amounts in their blood, urine, and tissues (up to 9 mg/100 ml of blood and 100 mg/l of urine).

The kidneys have a definite capacity to eliminate mercury, so that accumulation takes place only when the absorption rate exceeds this capacity. In the United States, it is considered that concentrations below 1.0 mg/10 m^3 of air can be completely eliminated; for concentrations greater than 1.0 mg, some mercury is retained temporarily in tissue combinations, while in very high concentrations, for example, as high as 10 mg, the characteristic symptoms of toxicity and the rates of elimination are apt to be variable.$^{(A-51)}$ It is not rare to find industrially exposed workers who excrete 2 mg of mercury daily, or even more, without exhibiting signs of mercurialism.

Limits for Mercury in Industrial Air. The bases for safe tolerance limits in industrial environmental air have recently been reviewed and questioned by Goldwater et al.(A-54) The current tolerance level for inorganic mercury of 0.1 mg/m^3 is based on studies in the felt-hat industry made by the United States Public Health Service, the results of which were published in 1941, and on the unpublished data communicated to the Committee on Threshold Limits of the American Conference of Governmental Industrial Hygienists (ACGIH). In the felt-hat study, 3 out of 66 men with mercury exposure of less than 0.08 mg/m^3 of air were classified as "borderline" cases of poisoning and 15 out of 127 with exposure of 0.08 to 0.15 mg/m^3 as "borderline" or "first stage". It is stated in the report "that the lowest atmospheric concentration for which a case of mercurialism was recorded was 1.0 mg mercury per 10 m of air", or 0.1 mg/m^3.

Buckel' [see Reference (A-54)] found in the urine of 172 men in a thermometer workshop "up to 10 times as much mercury in a day as could possibly be absorbed through the atmosphere". He attributed this to skin absorption. He recommends that atmospheric mercury never be permitted to exceed 0.075 mg/m^3. Prior to the study cited above, which apparently has served as the principal basis for the present tolerance limit for inorganic mercury, the United States Public Health Service also investigated the hatters' fur-cutting industry. The work was done in 1935 and published in 1937. In this study, six of 107 persons exposed to mercury vapor in concentrations of less than 0.1 mg/m^3 were diagnosed as having mercurialism.

The tolerance limit of 0.01 mg/m^3 for organic compounds of mercury as given by the ACGIH is based on five cases of methyl mercury poisoning reported by Ahlmark in 1948 and eight cases of poisoning due to alkyl mercury compounds reported by Lundgren and Swensson in 1949 [see Reference (A-54)]. Neither of these reports contains any data on atmospheric concentrations of mercury. Ahlmark suggests that "a percentage higher than 0.01 mg per cu m of methyl mercury compounds should not be allowed". Presumably, he means 0.01 mg of methyl mercury compounds per cubic meter of air. Thus, limits for mercury in industrial air, although apparently safe, have not been well substantiated.

Limits in Water. Drinking-water standards of the USPHS and WHO do not include limits for mercury(A-68), but for over a decade the maximum permissible concentration of mercury or mercuric ion in the U.S.S.R. has been 0.005 mg/l.

Limits in Foods. Mercury is present in food, the normal daily diet containing approximately 20 µg.(A-41) Mercury can be found in many foods in concentrations up to 10 µg/100 gm fresh weight.(A-64) FAO and WHO set a tolerance limit for mercury content of food at 50 µg/g.(A-66) In this country, the Government sets limits on the amount of food additives and pesticide residues allowable in food, but not levels for trace elements.(A-39, A-47)

Limits in Drugs. Brown [Reference (A-41), p 18] reviews the literature on reactions to organic mercurial compounds and comments on the fact that there are no satisfactory data on which to assess the risk. Except for hypersensitivity reactions, toxicity to clinical mercurial diuretics is relatively rare.

Environmental Hazards

A considerable amount of mercury is discharged into our environment each year either from commercial products or as waste. Currently, our national production is approximately 6 million pounds per year. During the 20th century, mercury consumption in the United States has totalled about 163,000,000 pounds, representing about 0.8 pound per capita (present population). In contrast to the concern about other contaminants – smoke, smog, and other air pollutants – little information is available on the amount of mercury accumulating in our environment.

Mercury may naturally accumulate in some part of our food chain. Minamata Bay in Japan appeared to be an example in which industrial wastes containing mercury had been discharged into a bay and mercury had accumulated in fish eaten by people.(A-59,A-60) More recently, a Japanese report indicates that a bacterial species can concentrate environmental mercury in its protoplasm 10^7 times.(A-44) Mercury is toxic to various plants, especially roses. In Sweden, mercury has been found in birds, fish, and other foodstuffs.(A-66) A Russian report investigated the accumulation of mercury by the larvae of aquatic insects.(A-50)

In this country, mercury has not been measured in our air- and water-monitoring systems(A-72). Mercury toxicity in water supplies has been known, however.(A-68) Trace elements in food, including mercury, have been also known for years(A-43), and the increase of mercury in foods due to the use of pesticides has been of concern, especially in Sweden. There are numerous recent reports of mercury accumulation in plants treated with mercurial pesticides. Woodwell(A-74) recently reviewed the ecology of DDT in plants, animals, air, water, and soil, and a corresponding study should probably be made for mercury.

Inasmuch as it is unlikely that mercury ore in its natural setting contributes substantially to the atmospheric load of mercury, all mercury in our environment is very likely a result of man's technology. Thus, mercury reaching man comes from these possible sources:

(1) Industrial-processing exposures to man

(2) Industrial waste and pollution – air and water – to man, plants, and animals

(3) Use patterns – paints, pesticides in food, drugs

(4) Natural concentration processes leading to the occurrence in plant and animal foods

> Minamata Bay poisoning with possible bacterial concentrations to plant or aquatic fauna buildup to fish to man

(5) Disposal sources – landfill, leaching

(6) Storage of ores awaiting refinement, product storage, etc.

(7) Other human sources.

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APPENDIX B

VANADIUM

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APPENDIX B

VANADIUM

Economics Information

Natural Occurrence(B-1, B-2, B-3)*

Six important primary minerals containing vanadium are:

Patronite from Peru:

Mixed sulfides, VS_2, V_2S_5

Carnotite from western Colorado, eastern Utah, south Australia, and Pennsylvania:

$K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$

Roscoelite from western Colorado and Utah:

$2\,K_2O \cdot 2Al_2O_3 \cdot (MgFe)O \cdot 3V_2O_5 \cdot 10SiO_2 \cdot 4H_2O$

Mottramite from South West Africa:

$5(CuPb)O \cdot V_2O_5 \cdot 2H_2O$

Vanadinite from Mexico, New Mexico, and Arizona:

$3PbO \cdot V_2O_5 \cdot PbCl_2$

Descloizite from Rhodesia, New Mexico, and Arizona:

$4(Pb \cdot Zn)O \cdot V_2O_5 \cdot H_2O$.

The ashes of bitumens, asphalts, and coals may yield up to 12 percent vanadium. Some fuel oils contain the element which was presumably derived from marine organisms that were precursors in the formation of petroleum. Vanadium occurs in the blood of holothurians, ascidians, and other aquatic animals. The oceans contain traces of the element, representing in total about 7,500 million metric tons of vanadium. The beet root, the vine, the beech, and the oak also contain traces. Vanadium has also been detected in meteorites and in the spectrum of numerous stars as well as that of the sun.

Estimated reserves in the United States total about 600,000 tons of contained vanadium metal – more than triple the projected 40-year demand. Deposits abroad may contain another 400,000 tons. In addition, very large tonnages may exist in various types of minerals that currently are not conventional sources.

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*References for Appendix B will be found on p B-18.

Domestic Production(B-1, B-4)

Statistics on domestic production of vanadium ore and vanadium pentoxide during the last decade are shown in the accompanying tables. The area of greatest mining activity – largely of carnotite – is the Colorado Plateau, comprising chiefly southwestern Colorado and southeastern Utah, and extending into northern Arizona and northern New Mexico. Some ore has also been produced in South Dakota and Wyoming. Vanadium from these sources has usually been a by-product or coproduct of uranium. In addition to production shown in the tables, the available domestic supply was augmented by 1,282 tons of vanadium contained in Atomic Energy Commission stocks of vanadium pentoxide.

Mills that recovered vanadium in 1965 from uranium-vanadium ores were:

Name	Location
American Metal Climax, Incorporated	Grand Junction, Colorado
Mines Development, Incorporated	Edgemont, South Dakota
Union Carbide	Rifle, Colorado
Vanadium Corporation of America	Shiprock, New Mexico

The Rifle mine of Union Carbide Corporation started production of vanadium in February, 1965. Also, Union Carbide is about ready to start production of vanadium pentoxide at its new plant in Wilson Springs, Arkansas, with an expected capacity of 1000 tons of ore processing per day. Vanadium Corporation of America is planning a vanadium facility in the Midwest to handle feedstocks imported from South Africa and elsewhere. Atlas Minerals has installed a vanadium unit at its Moab, Utah, uranium operation.

During 1965, Oregon Metallurgical Corporation and Vanadium Corporation of America reported production of high-purity vanadium and the alloying grade of 90 percent vanadium content.

Vanadium from ferrophosphorus, a by-product of the production of elemental phosphorus from Idaho phosphate rock was recovered by:

Name	Location
Kerr-McGee Corporation	Soda Springs, Idaho
Vitro Chemical Company	Salt Lake City, Utah
Susquehanna Western Corporation, and Mineral Engineering Company (FMC)	Garfield, Utah

The installation at Garfield, Utah, produces 99.5 percent vanadium pentoxide from FMC's phosphorus-plant slag located at Pocatello, Idaho. Mines Development Incorporated, is putting in a vanadium-processing-line at its Edgemont, South Dakota, plant to produce annually 1.5 million pounds of vanadium pentoxide from imported steel slag.

Ferrovanadium was produced in the United States principally by Reading Alloys Company, Incorporated, Shield Alloy Corporation, Union Carbide Corporation, and Vanadium Corporation of America.

TABLE B-1. SALIENT VANADIUM STATISTICS

Short Tons of Contained Vanadium

	1956-60 (Average)	1961	1962	1963	1964	1965
United States:						
Production:						
Ore and concentrate:						
Recoverable vanadium[(a)]	3,856	5,343	5,211	3,862[(b)]	4,362	5,226
Value, thousands of dollars	(b)	19,076	18,605	13,788	13,061	18,284
Vanadium pentoxide recovered	3,985	5,817	4,750	3,897	5,049	6,100
Consumption		2,015	2,314	2,906	3,550	4,708
Imports:						
Ferrovanadium (gross weight)	6	--	88	442	466	51
Ore and concentrate	1	--	--	--	111	--
Exports:						
Ferrovanadium and other vanadium alloying materials (gross weight)	133	120	201	183	103	220
Vanadium ores, concentrates, oxides, and vanadates	1,398	2,081	1,021	536	1,231	928
World: Production	5,059	8,722[(b)]	8,264	7,161[(b)]	7,841[(b)]	9,150

(a) Measured by receipts of uranium and vanadium ores and concentrates at mills plus vanadium recovered from ferrophosphorus derived from domestic phosphate rock.

(b) Revised.

(c) Withheld to avoid disclosing individual company confidential data.

TABLE B-2. RECOVERABLE VANADIUM OF DOMESTIC ORIGIN PRODUCED IN THE UNITED STATES, BY STATES

Short Tons of Contained Vanadium

State	1956-60 (Average)	1961	1962	1963	1964	1965
Colorado	3,059	4,149	3,742	3,047	3,312	4,017
Utah	486	514	525	382	405	387
Arizona and other States[(a)]	311	680	944	433[(b)]	645	822
Total	3,856	5,343	5,211	3,862[(b)]	4,362	5,226

(a) Includes Idaho, 1961-65; Montana, 1957; New Mexico, 1956-65; North Dakota, 1965; South Dakota, 1960-65; Wyoming, 1956-58, 1960-65; Oregon, 1964.

(b) Revised.

TABLE B-3. MINE PRODUCTION AND RECOVERABLE VANADIUM OF DOMESTIC ORIGIN PRODUCED IN THE UNITED STATES

Short Tons

Year	Mine Production(a)	Recoverable Vanadium(b)
1956-60 (average)	7,127	3,856
1961	6,359	5,343
1962	7,647	5,211
1963	6,047	3,862(c)
1964	5,184	4,362
1965	5,641	5,226

(a) Measured by receipts of uranium and vanadium ores and concentrates at mills, vanadium content.

(b) Recoverable vanadium contained in uranium and vanadium ores and concentrates received at mills, plus vanadium recovered from ferrophosphorus derived from domestic phosphate rock.

(c) Revised.

TABLE B-4. PRODUCTION OF VANADIUM PENTOXIDE IN THE UNITED STATES

Short Tons

Year	Gross Weight	V_2O_5 Content
1956-60 (average)	7,866	7,116
1961	10,796	10,387
1962	8,955	8,483
1963	7,347	6,959
1964	9,775	9,013
1965	11,498	10,996

Recovery Methods(B-2, B-5)

Vanadium is extracted from its principal ores and by-product sources by roasting the crushed ore with common salt at 850 C to sodium vanadate, usually in multiple-hearth furnaces. The furnace product is converted to sodium metavanadate by a water leach and subsequent addition of sulfuric acid to the leach liquor. Heating and stirring cause the precipitation of sodium hexavanadate. This so-called "red cake" is separated by filtration, washed, and fused in a direct flame to give a crude product containing about 90 percent vanadium pentoxide with contaminants such as iron, silicon, and molybdenum. The crude material is quite suitable for making ferrovanadium and various vanadium compounds. If this grade of pentoxide is redissolved in caustic-soda solution, the vanadium can be precipitated as ammonium metavanadate by the addition of ammonium chloride; on calcining the metavanadate, a pure form of vanadium pentoxide, is obtained suitable for reduction to vanadium metal.

In the recovery of vanadium from carnotite, the salt roast is quenched in sodium carbonate solution, which easily dissolves about 80 percent of the vanadium. Uranium is precipitated by adjusting the pH with sulfuric acid and boiling to remove the carbon dioxide. The vanadium remains in the filtrate and can be obtained as pentoxide by the "red cake" precipitation method. By another process for separating the metals in carnotite, an acid leach follows ore crushing, the salt wash is omitted and an ion-exchange technique is utilized.

Most of the pentoxide prepared from ores is used to make ferrovanadium containing 30 to 85 percent vanadium, for incorporation in steel. The ferrovanadium can be obtained through a reduction process by rapidly heating a mixture of pentoxide, iron oxide, carbon, and fluxes in an electric furnace; alternatively, aluminum or ferrosilicon can be employed in place of carbon as a reducing agent.

The reduction of vanadium pentoxide, ferrovanadium, vanadium chloride, and vanadic acid to metal (99. 8 percent purity) can be achieved by using calcium or calcium and iodine in an inert atmosphere at elevated temperatures. A list is attached of domestic suppliers of vanadium and vanadium raw material.

Exposures to the pentoxide and vanadates in mining and milling operations, and to the crushing, grinding, and packing of basic slag containing vanadium, have all led to cases of vanadium poisoning. Probably most adverse results of this nature could be avoided by controlling contamination of the air so that the vanadium pentoxide dust content does not exceed 0. 5 mg/m^3 of air, or 0. 1 mg/m^3 for the pentoxide as fume.

The following is a list of some of the United State suppliers of vanadium and vanadium compounds:

Vanadium Suppliers

Associated Metals & Minerals Corporation, New York
Belmont Smelting & Refining Works, Incorporated, Brooklyn, New York
Brandeis, Goldschmidt & Company, Incorporated, New York
Frankel Company, Incorporated, Detroit, Michigan
Fred H. Lenway and Company, Incorporated, San Francisco, California
Metal Traders, Incorporated, New York
Philipp Brothers, New York
United Mineral & Chemical Corporation, New York
Vanadium Corporation of America, New York

Vanadium Alloys Suppliers

Belmont Smelting & Refining Works, Incorporated, Brooklyn, New York
Brandeis, Goldschmidt & Company, Incorporated, New York
Mercer Alloys Corporation, Greenville, Pennsylvania
Vanadium Corporation of America, New York

Vanadium Ore Suppliers

Brandeis, Goldschmidt & Company, Incorporated, New York
Fred H. Lenway and Company, Incorporated, San Francisco, California
Metal Traders, Incorporated, New York
Philipp Brothers, New York

Vanadium Pentoxide Suppliers

American Metal Climax, Incorporated, New York
Brandeis, Goldschmidt & Company, Incorporated, New York
Fred H. Lenway and Company, Incoroporated, San Francisco, California
Mercer Alloys Corporation, Greenville, Pennsylvania
Metal Traders, Incorporated, New York
Philipp Brothers, New York
C. Tennant, Sans & Company of New York, New York
Vanadium Corporation of America, New York

Use Pattern(B-1)

In 1965, domestic consumption of vanadium increased 33 percent from 1964 for all uses. As indicated in Table B-5, total consumption was 4,708 tons, of which all uses but 197 tons for chemicals were in metallurgical applications.

TABLE B-5. VANADIUM CONSUMED IN THE UNITED STATES IN 1965 ACCORDING TO USE

Use	Consumption, short tons
Steel:	
High-speed	304
Hot-work tool	115
Other tool	116
Stainless	32
Other alloy(a)	2,830
Carbon	656
Total steel	4,053
Gray and malleable castings	35
Nonferrous alloys(b)	351
Chemicals	197
Other(c)	72
Grand total	4,708

(a) Includes some vanadium used in high-speed or other tool steels not specifed by reporting firms.

(b) Principally titanium-base alloys.

(c) Principally high-temperature alloys, welding rods, cutting and wear-resistant materials.

A preliminary estimate for 1966 indicates a total consumption of 5,660 tons of vanadium, broken down as follows:

4,754 tons or 84 percent for ferrous alloys
622 tons, or 11 percent for nonferrous alloys, especially titanium and aluminum
284 tons, or 5 percent for chemical and catalytic uses.

The 1966 figure indicates that U. S. consumption of vanadium has nearly tripled since 1961. Increases in the future consumption of vanadium are expected to result from increasing ferroalloy requirements. The total vanadium consumption 40 years hence is estimated at about 4 times what it is today, with major consumption still in the the steel industry.

Individual categories of vanadium consumption are discussed below:

Steel. (B-1, B-6) Increased use of vanadium in 1965 by the steel industry has been primarily in:

- High-strength, low-alloy steels
- Line and oil-drill pipes
- Heavy forgings
- Deep-drawing steels by the continuous-casting process.

Currently, about 82 percent of the vanadium is consumed as ferrovanadium and carbon-vanadium alloys in the manufacture of tool steels, engineering steels, high-strength structural steels, nonaging rimming steels, and special wear-resistant cast irons. A satisfactory ferrovanadium alloy contains 30 to 40 percent of vanadium and not more than about 0.5 percent carbon, 1 percent silicon, 2 percent aluminum, 0.1 percent phosphorus, and 0.1 percent sulfur. In steel fabrication, vanadium functions in three ways: (1) it increases strength and durability by partially dissolving the ferrite, (2) it produces a finer and more uniform grain size and minimizes the tendency for grain growth during heat treatment (3) it forms very stable carbides that add to strength and hardness and show very little tendency to segregate or to form large masses at elevated temperatures.

Quantities ranging from about 0.05 to 0.5 percent of vanadium are effective for the fabrication of vanadium constructional steels of four major types (Table B-6). Certain more complex alloy types contain 1 to 2 percent or even more of vanadium, along with nickel, chromium, molybdenum, or manganese. The vanadium content and uses of 13 types of vanadium tool steels are also shown (Table B-7). As can be seen, the vanadium content of high-speed tools ranges to over 2 percent.

TABLE B-6. VANADIUM CONSTRUCTIONAL STEELS, COMPOSITIONS FOR USES

Type	Vanadium Content, %	Use
C-V	0.10-0.20	RR equipment, shafts, arms, connecting rods, driving axles, crank pins, guides, piston rods. Also parts for heavy machinery, pumps, diesel engines.
Cr-V	0.05-0.50	Low carbon: carburized gears, camshafts, piston pins. Pressure vessels, tubing. Stampings Medium carbon: axles, shafts, steering arms, gears, springs. Arbors, spindles, shafting. Cyanided gears, bolts, washers, forgings. High carbon: tools, ball bearings, wearing plates.
Mn-V	0.05-0.20	Heavy forgings, plates for transportation equipment and for tanks. Also for rivets, bolts, etc.
V-spring steels	0.08-0.2	Heavy and light springs for transportation equipment and heavy machinery apparatus and instruments. Automotive springs.

TABLE B-7. CLASSIFICATION OF TOOL STEELS

Type	Type	Vanadium Content, %	Total Alloy Content, %	Purpose
1	Carbon tool steel	--	--	General purpose
2	Carbon-V tool	0.08-0.40	0.08-0.40	General purpose
3	Low-Cr and Cr-V tool	0.10-0.20	0.20-1.40	Substitutes for carbon tool steels
4	Low-W, high-C tool and die	0.10-0.25	1.45-3.50	Finishing tools for hard steels and nonferrous alloys
5	Mn oil hard die (nondeforming)	0.10-0.25	1.70-3.50	General purpose tools, espc. dies, punches, broaches
6	W chisel and punch	0.10-0.30	2.45-4.80	Shears, battering tools, heading dies
7	W finishing tool and die	--	3.40-7.50	Hard and keen edge for cutting hard materials (brittle)
8	Si-Mn punch and chisel	0.15-0.30	1.60-3.30	Cold cutting
9	(a) High Cr, high-C punch and die	0.75-1.00	13.85-16.75	Rolls, mandrels, punches, dies, shears; cold work
	(b) High-Cr, high-C punch and die	0.80-1.00	14.30-24.80	Tougher than (a)
10	Cr hot-work die	--	3.65-4.85	Gripper, bending, heading dies; light work to 600 F
11	W hot-work die	0.30-1.20	9.55-24.70	Blanking, forming, extrusion, casting dies to 1100 F
12	W-Cr hot-work and die-casting die	0.20-0.60	6.60-17.60	Tougher than (11); same purposes
13	(a) High-speed (conventional)	0.75-2.25	17.65-28.65	Cutting tools, all types; severe hot work
	(b) High-speed (Mo)	0.75-2.50	11.25-18.50	Cutting tools, all types; less expensive than (a)
	(c) High-speed (Co)	0.75-2.25	20.25-41.75	Cutting tools, all types; cutting hard, gritty materials

Castings. In cast irons, vanadium is only occasionally used as the single alloying element; much greater use is made of the element in amounts of 0.05 and 0.20 percent, associated with one or more of nickel, molybdenum, chromium, and copper. Vanadium tends to limit graphitization and aids in effecting uniform graphite distribution and the production of graphite flakes of moderate size. Typical uses are diesel cylinder heads, die blocks, machine tools, and brake drums.

In cast steel, the vanadium content varies from about 0.05 to about 0.20 percent. The carbon content for cast constructional steels varies from about 0.20 up to 0.50 percent, in conjunction with various amounts of nickel, chromium, manganese, or molybdenum. Typical applications are for locomotive frames, heavy gears, housings, heavy transportation equipment, heavy-equipment dies, and turbines.

Nonferrous Alloys. (B-7) Consumption of 351 tons of vanadium in nonferrous alloys was reported for 1965. Ductile vanadium for the production of alloys is generally produced by calcium reduction of vanadium chloride in a closed bomb. The metal contains approximately 0.1 percent oxygen, 0.05 percent carbon, and 0.04 percent nitrogen. The metal can be purified further in a hot-wire or fused-salt bath.

Small additions of titanium and zirconium to purified vanadium show a strong scavenging action on the interstitial elements. Adding some of the more common metals such as iron, chromium, silicon, aluminum, molybdenum, and nickel to vanadium greatly improves tensile strengths with little elongation or reduction in area. The addition of zirconium or titanium leads to alloys of high tensile strength, increase in elongation, and a reduction in area. Vanadium also alloys with such metals as columbium, niobium, rhenium, tantalum, and tungsten. Many of these alloys have phenomenal tensile strengths and excellent chemical-corrosion resistance over a wide range of oxidizing and reducing conditions. Alloys of vanadium and hafnium have been evaluated for possible use in atomic reactors.

Copper-vanadium alloy of about 3 percent vanadium content has been used for the control of gases and microstructure in a number of copper-base alloys. Vanadium has also been added with either silicon or nickel to achieve desired thermal-expansion rates combined with good strength properties in aluminum-alloy pistons in internal-combustion engines.

Electrochemical Systems. A primary battery containing a zinc anode and a vanadium pentoxide cathode that uses an electrolyte consisting of ammonium hydroxide, ethylene glycol, and boric acid, is available commercially as a bias cell providing stable voltage at low current over long periods. An experimental primary cell containing a silver anode and a vanadium pentoxide cathode uses a silver iodide electrolyte. This is typical of a variety of primary systems that could be made commercially if applications warrant.

Catalysts and Chemicals. (B-9 – B-14) 1965 consumption of vanadium in chemicals is reported to have been only 197 tons. This figure includes such items as:

- Production of sulfuric acid
- Manufacture of phthalic anhydride

- Manufacture of maleic anhydride
- Production of aniline black
- Oxidation of cyclohexanol to adipic acid
- Oxidation of ethylene to acetaldehyde
- Oxidation of anthracene to anthraquinone
- Oxidation of toluene or xylene to aromatic acids
- Oxidation of furfural to fumaric acid
- Oxidation of hydroquinone to quinone
- Oxidation of butene-2 and 1,3-butadiene to maleic anhydride
- Ammoxidation of toluene, m-xylene, p-xylene, and propylene
- Preparation of vinyl acetate from ethylene
- Manufacture of cyclohexylamine from cyclohexanol and ammonia
- Catalytic combustion of exhaust gases
- Catalytic synthesis of ethylene-propylene rubbers.

One of the major uses of vanadium pentoxide is as a catalyst in preparing sulfuric acid. Vanadium or its compounds, especially the pentoxide on asbestos as carrier, have been used. Also, vanadium can be employed in solid beds that range from 20 to 50 inches in depth, supported on a screen placed over a cast-iron or steel grill. Approximately 25,000,000 short tons of sulfuric acid are manufactured annually in the United States. It is estimated that about 20,000,000 tons of this is produced employing 1,900,000 lb of vanadia catalyst containing about 8 percent vanadium pentoxide, or 76 tons of vanadium pentoxide.

Manufacturers/distributors of sulfuric acid are:

Alcan Sales
Allied Chemical, B & A Products
American Cyanamid
American Smelting & Refining
American Zinc, Lead & Smelting
Arkla Chemical
Armour Industrial Nitrogen Division
H. J. Baker & Brother (Distributor)
J. T. Baker Chemical
Central Chemical Division,
  Wilson & Company
Chemtech Corporation (Distributor)
Chevron Chemical, Ortho Division
Collier Carbon & Chemical
Davison Chemical Division
Du Pont, Industrial Division
Eagle-Picher
Essex Chemical, Chemicals Division
W. R. Grace, Nitrogen Products
Gulf Oil, Chemicals Department
Hill Brothers Chemical (Distributor)
Inland Chemical (Distributor)
International Minerals & Chemical
Jones Chemicals (Distributor)
Kerr-McGee
E & F King & Company (Distributor)
Mallinckrodt Chemical Works
McKesson & Robbins (Distributor)
Mississippi Chemical
Monsanto Company
National Zinc
Nitine, Incorporated
Octagon Process
Olin Mathieson Chemicals Division
Ozark-Mahoning
Pennsal Chemicals
Pioneer Chemical
Prior Chemical (Distributor)
Reichhold Chemicals
Rohm & Haas
H. M. Royal, Incorporated (Distributor)
Rumford Chemical Works
Smith-Douglas
Stauffer Chemical, Industrial Chemical
  Division
Stauffer Chemical, Consolidated Chemicals
  Division
Tennessee Corporation, Industrial
  Chemicals
Texas Gulf Sulphur
Textile Chemical (Distributor)
Thompson-Hayward Chemical (Distributor)

Titanium Pigment
United States Steel
USI Chemicals
Vulcan Materials, Chemical Division
Wright Chemical

Two closely related processes involving the use of vanadia are the oxidation of aromatic hydrocarbons to phthalic anhydride and the oxidation of benzene to maleic anhydride. Phthalic anhydride capacity is approximately 700,000,000 lb and maleic anhydride 175,000,000 lb. The total annual market for vanadia catalysts for phthalic and maleic is probably 700,000 lb. Assuming a vanadia content of 6 percent, this amounts to 21 tons of vanadia.

Manufacturers/distributors of maleic and phthalic anhydride are:

Maleic Anhydride

Allied Chemical, Plastics Division
Borden Chemical
Chevron Chemical, Oronite Division
Heyden Division
Koppers Company
Monsanto Company
Petro-Tex Chemical
Prior Chemical (Distributor)
Reichhold Chemicals
Samincorp (Distributor)
United States Steel

Phthalic Anhydride

Allied Chemical, B & A Products
Allied Chemical, Plastics Division
J. T. Baker Chemical
Browing Chemical (Distributor)
Chevron Chemical Oronite Division
Ciba Products
Conray Products (Distributor)
Fallek Chemical (Distributor)
Fallek Products (Distributor)
M. W. Hardy & Company (Distributor)
Hatco Chemical, W. R. Grace & Company
Heyden Division
International Chemical (Distributor)
International Selling (Distributor)
Koppers Company
Monsanto Company
Puerto Rico Chemical
Reichhold Chemicals
Sherwin-Williams
Stepan Chemical
Tar Residuals (Distributor)
Toyo Koatsu Industries
Union Carbide Chemicals Division
United States Steel
Witco Chemical, Organics Division

It is believed that considerable ammonium metavanadate is still used in the manufacture of adipic acid. Catalytic oxidation of cyclohexanol or cyclohexanone with nitric acid in the liquid phase produces adipic acid. The reaction is usually catalyzed by ammonium metavanadate. Most of the catalyst is not recovered. Although several alternative routes have been developed for synthesis of adipic acid, the use of ammonium metavanadate to prepare only a moderate amount of the 800,000,000 lb annual quantity would consume 5 to 10 tons of catalyst.

Vanadium Corporation of America completed a new plant in 1965 to produce vanadium oxytrichloride for use as a catalyst in producing ethylene-propylene synthetic rubbers. Earlier, Stauffer started producing pilot quantities of both the tetrachloride and trichloride of vanadium for use in stereospecific catalyst systems and as intermediates for making high-purity metals and intermetallics. The tetrachloride, moreover, is suggested for use as a chlorinating agent.

In dye manufacture and dyeing, vanadium compounds are widely used in the production of aniline black. Vanadium salts are added as catalysts to a mixture of aniline and aniline hydrochloride and potassium or sodium chlorate. Other black and brown aniline colors can be obtained by oxidizing substituted anilines.

Vanadium compounds are also used as mordants for the dyeing and printing of cotton, and particularly for fixing aniline black on silk. Ammonium metavanadate has been used as a catalyst in the dyeing of leather and fur. Some of the modern quick-drying inks depend for their performance upon the addition of ammonium metavanadate.

Various vanadium compounds, such as resinates, naphthenates, and linoleates, formerly used as driers in paints and varnishes and in making lusters for pottery, procelain, and glass, have been replaced by other metallic salts. A new gasoline additive that is said to eliminate smog components from automobile exhaust gases has been developed by Addit Corporation, Dearborn, Michigan. It is a vanadium pentoxide-organometallic compound diffused in a liquid mixture. The use of vanadium carbonyls as catalysts, plating agents, and fuel additives is being explored.

Commercially available vanadium compounds are:

Vanadium metal
Vanadium acetate
Vanadium acetylacetonate
Vanadium carbide
Vanadium chloride
Vanadium diboride
Vanadium disilicide
Vanadium ethylsulfate
Vanadium naphthenate
Vanadium oxalate
Vanadium pentoxide
Vanadium sesquioxide
Vanadium silicate
Vanadium sulfate
Vanadium tetrachloride
Vanadium tetroxide
Vanadium trichloride
Vanadium trifluoride.

Manufacturers/distributors of vanadium compounds used in chemical areas include:

Vanadium Acetylacetonate

Aceto Chemical
Atomergic Chemetals
MacKenzie Chemical Works
Shepherd Chemical
Stauffer Chemical, Specialty Chemical Division
Troy Chemical

Vanadium Carbide

Atlantic Equipment Engineers
Atomergic Chemetals
Cerac, Incorporated
Consolidated Astronautics
Electronic Space Products
Kerr-McGee
Shieldalloy Corporation
Var-Lac-Oid Chemical

Vanadium Dichloride

Atomergic Chemetals
Electronic Space Products
Magnesium Elektron (Distributor)
Rocky Mountain Research
Vanadium Corporation of America

Vanadium Metal

Atlantic Equipment Engineers
Atomergic Chemetals
Belmont Smelting & Refining Works
Bram Metallurgical-Chemical
Cerac, Incorporated
Consolidated Astronautics
Electronic Space Products
Materials Research
Shieldalloy Corporation
Union Carbide Mining & Metals Division
United Mineral & Chemical
Vanadium Corporation of America
Var-Lac-Oid Chemical

Vanadium Oxytrichloride

Atomergic Chemetals
Magnesium Elektron (Distributor)
Rocky Mountain Research
Stauffer Chemical, Specialty Chemical Division
Union Carbide, Mining & Metals Division
Vanadium Corporation of America
Var-Lac-Oid Chemical

Vanadium Pentoxide (Vanadic Acid Anhydride)

Atlantic Equipment Engineers
Atomergic Chemetals
J. T. Baker Chemical
Cerac, Incorporated
Electronic Space Products
Kerr-McGee
Union Carbide, Mining & Metals Division
Vanadium Corporation of America
Var-Lac-Oid Chemical

Vanadium Sulfate (Vanadyl Sulfate)

Atomergic Chemetals
Chemical Commerce
Electronic Space Products
Vanadium Corporation of America

Vanadium Tetrachloride

Atomergic Chemetals
Electronic Space Products
Rocky Mountain Research
Stauffer Chemical, Specialty Chemical Division
Union Carbide, Mining & Metals Division
Vanadium Corporation of America

Vanadium Tetroxide

Atomergic Chemetals
Electronic Space Products
Rocky Mountain Research

Vanadyl Acetate

Atomergic Chemetals
Var-Lac-Oid Chemical

Vanadyl Acetonate

Atomergic Chemetals
Troy Chemical
Var-Lac-Oid Chemical

Vanadyl Oxalate

Atomergic Chemetals
Rocky Mountain Research

Vanadyl Sulfate

Atomergic Chemetals
Vanadium Corporation of America

Glass and Ceramics.(B-15) Compounds of vanadium are used in the ceramic industry for glazes and enamels. Vanadium pentoxide is used in clear glass to absorb ultraviolet rays. Vanadium pentoxide is an excellent flux, and small amounts may be helpful in promoting vitrification of ceramic products. When vanadium is present as the trioxide, the glass does not absorb ultraviolet rays. Vanadium tetroxide forms special refractories with beryllium oxide.

Wear-Resistant Facings. Hard and special materials, e.g., vanadium boride, vanadium carbide, vanadium nitride, and vanadium silicide, are used in the tool and die industry, for electrodes, in gas turbines, and for many applications in which hardness is required.

Magnets.(B-16) Ductile alloys of iron-cobalt-vanadium called Vicalloys were developed in this country in 1938. A very high degree of permanent-magnet quality can be produced in hard-drawn wires of these alloys when properly heat treated. Vicalloy has been used for the high-quality recording of sound. The binary alloy (50 percent iron, 50 percent cobalt) Permendur is magnetized very readily to very high inductions with moderate field strengths, but the alloy can only be worked while hot. The addition of about 2 percent vanadium, molybdenum, or chromium increases resistivity and makes it possible to obtain cold workability. 2 V Permendur and Hiperco are examples of this type of alloy. These materials find application in pole tips for magnets, receiver diaphragms, and high-flux-density motors.

Recent Research

Recent research in vanadium has led to the following developments:

(1) Studies by the Bureau of Mines showed approximately 0.27 weight percent solubility of carbon in electrorefined vanadium at the eutectic temperature, 1,650 C, and 0.03 at 700 C.

(2) Electrorefined vanadium in the temperature range of 77 to 273 K was evaluated as to tensile properties and the effects of interstitial impurities.

(3) Vanadium metal of 99.95 percent purity was prepared by electrorefining commercial vanadium metal in a molten sodium bromide, potassium bromide, and vanadium bromide electrolyte.

(4) Commercial high-purity vanadium metal was evaluated for susceptibility to stress-corrosion cracking in different acids and corrosive salts.

(5) The hafnium-vanadium system was the subject of study by the Bureau of Mines for possible use of these alloys in atomic reactors.

(6) Studies at the Argonne National Laboratory of the Atomic Energy Commission of a lithium hydride fuel cell for use with a reactor suggested that high-purity vanadium metal would be the best diaphragm material.

(7) Investigations at Oregon State University showed that vanadium pentoxide behaves in a manner similar to manganese dioxide as a cathode in electrochemical cells.

(8) Personnel at Ames Laboratory of the Atomic Energy Commission investigated hydrogen embrittlement at surfaces of vanadium.

(9) Patents were issued on:

- Vanadium-alloy compositions
- Removing vanadiferous deposits from boiler tubes
- Catalysts and vanadium-extractive processes.

Toxicity Information

Vanadium toxicity has not been as extensively studied as mercury toxicity nor has it provided the hazards of mercury. However, there are several reviews, namely those of Hudson(B-21), Stockinger(B-26), Browning(B-18), Butterworth(B-19), and Sjoberg(B-25) that serve as the nucleus for toxicological data in this report. Except where otherwise indicated, the following information is drawn from these texts.

Incidence of Vanadium Poisoning

Dutton, in 1911, first described industrial poisoning from vanadium. He considered that this took the form of chronic intoxication, the chief impact being on the lungs, kidneys, and intestinal tract. Relatively few cases of vanadium toxicity are reported in the literature, and these are confined mainly to industrial settings. Hudson(B-21) reviewed several case reports citing those of Dutton, Wyers (1946 and 1948), Sjoberg (1950), Lewis (1959), Harris et al. (1959), and Archer et al. (1962). The cases of poisoning in the past were found mainly in the mining and refining of vanadium ore. Table B-8 shows the current potential occupation exposure hazards as listed by Gefafer(B-20).

TABLE B-8. POTENTIAL OCCUPATIONAL EXPOSURES(B-20)

Alloy makers	Petroleum refinery workers
Boiler cleaners	Photographic chemical makers
Ceramic makers	Textile dye workers
Dye makers	Uranium millers
Dyers	Vanadium alloy makers
Ferrovanadium workers	Vanadium millers
Glassmakers	Vanadium miners
Ink makers	Vanadium workers
Organic chemical synthesizers	

Pharmacology

Mechanism of Action. Vanadium exhibits a variety of biological activities, but only some of the mechanisms are known. It is considered to be an essential trace element in some plants and invertebrates. In the marine worm, Ascidia, vanadium occurs in blood as a chromoprotein, haemovanadium. In the haemovanadium form, vanadium provides the oxygen-carrying capacity of the blood, which is exemplary of its ability to participate in oxidation-reduction reactions.

Various enzyme systems have been shown to be affected by vanadium compounds. Some of these compounds reduce cholesterol blood levels and reduce cholesterol and phospholipid metabolism in the liver. Aortic plaques also have been reduced with the administration of vanadium compounds. The mechanism is apparently inhibition of the conversion of hydroxymethyl glutaric acid to methyl crotonic acid and blocking the utilization of mevalonic acid. Vanadium also inhibits the sulfhydryl-dependent succinic dehydrogenase of liver. Vanadium compounds have been shown to reduce the levels of cystine in hair and fingernails. Cystine levels of fingernails have been suggested as an early metabolic change in vanadium(B-24). In rats and rabbits, vanadium in conjunction with iron has been shown to have a beneficial hematopoietic effect on animals fed on anemia-producing diet.

Absorption, Distribution, and Excretion. Vanadium is toxic if sufficient quantity gains entrance to the body. Injected compounds are more readily absorbed and distributed than inhaled compounds. The usual route of industrial poisoning is by inhalation of dust or fumes. Vanadium is only moderately well absorbed from the gastrointestinal track. Therefore, ingestable forms are usually nontoxic. Oral vanadium is excreted largely by the kidney and from the bowel at a ratio of 5:1 urine over feces. Injected or inhaled vanadium is excreted largely by the urine. Retention of administered vanadium compounds is greatest in the liver and kidney, although significant quantities are retained by the skeleton. Levels of vanadium in the tissues of men who have not been exposed to vanadium is usually less than 1 mg/g of ashed material. Urinary and blood levels for exposed and unexposed subjects were presented by Vintinner(B-27) as shown in Table B-9.

TABLE B-9. VANADIUM CONTENT OF BLOOD AND URINE(B-27)

	Control Group	Inactive-Ore Group	Active-Ore Group
	Blood (Mg/100 Cc)		
Median	0.031	0.036	0.041
Maximum	0.060	0.093	0.060
	Urine (Mg/Liter)		
Median	0.016	0.017	0.041
Maximum	0.060	0.110	0.298

Toxic Dosages in Animals and Man. Lethal dosages of vanadium differ somewhat according to the material and species. Table B-10 summarizes levels of toxicity for various compounds and species.

Men receiving 20-mg of vanadium pentoxide (V_2O_5) as sodium tetravandate intravenously were observed to show at various times salivation, lacrimation, disappearance of the pulse, cessation of respiration, diarrhea and fall in temperature up to 3 degrees. Thirty mg of the material is thought to be a fatal dosage to a man weighing 70 kg.

TABLE B-10. LETHAL DOSES(B-21)

MgV_2O_5/kg

Compound	Rabbit	Guinea Pig	Rat	Mouse
Colloidal, V_2O_5	1-2	20-28		87.5-117.5
Ammonium metavanadate	1.5-2.0	1-2	20-30	25-30
Sodium orthovanadate	2-3	1-2	50-60	50-100
Sodium pyrovanadate	3-4	1-2	40-50	50-100
Sodium tetravanadate	6-8	18-20	30-40	25-50
Sodium hexavanadate	30-40	40-50	40-50	100-150
Vanadyl sulphate	18-20	35-45	158-190	125-150
Sodium vanadite		30-40	10-20	100-150

Symptoms of Vanadium Poisoning. Acute vanadium poisoning in animals is characterized by marked nervous disturbance, hemorrhagic enteritis, and a fall in temperature. Death is preceded by paralysis of the hind legs, labored respiration, and convulsions. Chronic poisoning is similar to acute poisoning with the symptoms less marked.

Acute human symptomatology is usually associated with inhalation of dust, which produces irritant reactions of the mucous membranes of the eyes, nose, throat, and upper respiratory tract. These symptoms can progress to nasal catarrh, nose bleeding, bronchitis, pneumonia, nausea, vomiting, and abdominal pain. A greenish tongue is common among vanadium workers but is of no known toxicological significance. For the most part, the following symptoms have been described as characteristics of the effects of vanadium compounds: dyspnea, wheezing, cough, pallid skin, irritation of the conjunctiva, slight or copious nasal catarrh; sores in the nares; dryness or smarting of the nose and throat, tremor of the fingers and arms, and greenish-black discoloration of the tongue. Gefafer(B-20) also reported elevated blood pressure, palpitation on exertion, profuse bronchitis, bronchospasm, emaciation, and other symptoms.

Diagnosis and Treatment. The diagnosis of vanadium intoxication is usually made by knowledge of exposure, signs and symptoms of vanadium poisoning, and the finding of elevated levels of vanadium in the urine. A reduction of the cystine content of fingernails has been suggested as an early indication of vanadium exposure.(B-24) Treatment consists mainly of protecting the individual from further exposure and giving supportive therapy. Administered ascorbic acid has been protective in some animal studies but not clinically. BAL has not been found useful.

Tolerance Limits. Threshold limits of 0.5 mg of V_2O_5 dust/m^3 of air, and 0.1 mg/m^3 for fumes have been set by the American Conference of Governmental Industrial Hygienists.

Environmental Hazards

Vanadium has been measured in the Public Health Service's National Air Sampling Network, but the concentrations found have not indicated an air-pollution problem. Vanadium, outside of the industrial setting, has not been a reported problem, with one exception. Berg(B-17) describes vanadium contamination in phosphorus containing dietary supplements added to chick feed, which induced toxic responses with reduced production.

McKee and Wolf(B-23) reviewed briefly vanadium hazards relative to water quality criteria. Trace amounts of vanadium (0.02 to 0.15 mg/l) have been found in the waters of certain areas of New Mexico. Stokinger(B-26) reported a decreased incidence of coronary heart disease there. Vanadium in drinking water at concentrations of 0.03 to 0.22 mg/l reduced the incidence of dental caries in both primary and permanent teeth. Thus, although vanadium can be toxic to man, trace levels seem to be beneficial. However, we do not know what environmental hazard will be created by the accumulation of vanadium from industrial sources in air, soil, or water.

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APPENDIX C

NICKEL

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APPENDIX C

NICKEL(C-1, C-2)

Economics Information

Natural Occurrence

Nickel is a widely distributed and a relatively plentiful element comprising about 0.01 percent of igneous rocks. It is also present in some meteorites, and large quantities are believed to exist in the earth's core. The two commercially important nickel minerals are pentlandite $(Ni, Fe)_xS_y$ found in Ontario, and garnierite $(Ni, Mg)SiO_3 \cdot nH_2O$ found principally in New Caledonia. Other nickel minerals of less importance are the red nickel ore (NiAs); millerite, or yellow nickel ore (NiS); briethauptite (NiSb); niccolite, or white nickel ore $(NiAs_2)$; gersdorffite (NiAsS); and ullmannite (NiSbS). Sulfide ores also are fairly widely distributed in Europe and Asia, and some are present in South Africa and the United States. Some nickel silicate ore is found in Cuba. Generally, the arsenide and antimonide minerals are not important enough to be classed as commercial sources. Nickel in trace amounts is present in marine organisms. It has been estimated that there are about 2500 million metric tons of nickel in the oceans.

Production(C-3, C-4, C-5)

Primary Sources. Figures on world production of nickel by countries and nickel statistics on United States production are given in Tables C-1 and C-2.

In 1965, for the second successive year, world nickel production reached a record high - 472,000 tons, 12 percent above that of 1964. Major world producers, particularly International Nickel Company of Canada, Limited (InCo), Société Le Nickel, and Falcon-bridge Nickel Mines, Limited, were engaged in aggressive exploration and development programs in Canada, New Caledonia, Guatemala, and Greece. Kaiser Aluminum and Chemical Corporation and Société Le Nickel announced agreement jointly to produce nickel products and to market them in the United States, whose imports currently originate almost exclusively in Canada. Two new jointly owned companies were to be formed. One would own production facilities in New Caledonia to be operated by Le Nickel, and the other would be Kaiser Nickel Company, which would market ferronickel here and also refine nickel products. The first step in the program for New Caledonia would be installation of facilities to produce 35 million pounds of nickel as ferronickel.

The United States' only nickel mine, the Hanna Mining Company, Riddle, Oregon, supplied about 6 percent of the domestic needs in 1966.

In 1965, Hanna mined 1,140,000 dry tons of ore containing 16,188 tons of nickel. The company processed the ore into 26,246 tons of ferronickel containing 12,666 tons

TABLE C-1. WORLD PRODUCTION OF NICKEL BY COUNTRIES(a)

Short Tons

Country	1961	1962	1963	1964	1965(b)
North America:					
Canada(c)	232,991	232,242	217,030(d)	228,496(d)	268,837
Cuba:					
Content of oxide(e)	16,320	16,222	16,200	16,300	16,400(e)
Estimated content of sulfide	--	2,080	2,200	2,400	2,450(e)
United States:					
Byproduct of copper refining	625	648	707	949	844
Nickel recovered from domestic ore	10,551	10,569	10,725	11,236	12,666
South America: Brazil (content of ferronickel)	90(d)	260(d)	1,107(d)	1,100(e)	1,100(e)
Europe:					
Albania (content of nickeliferous ore(e)	3,900	4,600	3,300	3,900	4,000
Finland:					
Content of nickel sulfate	177	179	172	162(d)	180
Content of concentrates	2,239	2,715	3,230	3,494(d)	3,252
Germany, East (content of ore)(e)	110	110	110	110	110
Poland (content of ore)	1,453	1,458	1,218(d)	1,400(e)	1,400(e)
U. S. S. R. (content of ore)(e)	77,000	90,000	90,000	90,000	95,000
Africa:					
Morocco (content of cobalt ore)	284	316	302	336	330(e)
Rhodesia, Southern (content of ore)	64	86	131	191	770(e)
South Africa, Republic of (content of matte and refined nickel)(e)	2,900	2,700	2,700	2,700	3,000
Asia:					
Burma (content of speiss)	112	182	112	70(e)	70(e)
Indonesia (content of ore)	694	491	1,760	1,760	3,900(e)
Korea, South (content of ore)	31	29	29	20	20(e)
Oceania: New Caledonia (recoverable)(f)	48,600	28,775	37,920(d)	58,200(e)	57,400(e)
World total (estimate)	398,000	394,000	389,000(d)	423,000	472,000

(a) Compiled from data available May 1966.

(b) Preliminary.

(c) Comprises refined nickel and nickel in oxide produced and recoverable nickel in matte exported.

(d) Revised.

(e) Estimate.

(f) Comprises nickel-cobalt content of matte and ferronickel produced in New Caledonia plus recoverable nickel in ore exported. Mine production (nickel content of ore) was as follows: 1961, 58,800 tons; 1962, 37,500 tons; 1963, 49,000 tons; 1964, 65,300 tons; and 1965 (estimated), 88,400 tons.

of nickel. This excellent recovery was made possible by installation of a rotary dryer, air classifier, two multiple-hearth roasters (natural gas fired), and two transformers.

Nickel salts – mostly nickel sulfate – were produced as a by-product of copper refining at Carteret and Barber, New Jersey; Laurel Hill, New York; Baltimore, Maryland; Tacoma, Washington; and El Paso, Texas. The nickel content of salt production was 844 tons, and of shipments, 739 tons.

In addition, chemical companies produced salts containing 3,442 tons of nickel and shipped 2,815 tons. Raw materials comprised both new and scrap metal. Thus, nickel content of total salts production in 1965 was 4,286 tons.

TABLE C-2. SALIENT NICKEL STATISTICS

Short Tons

	1956-60 (Average)	1961	1962	1963	1964	1965
United States						
Mine production	12,247	13,133	13,110	13,394	15,420	16,188
Plant production:						
Primary	10,888	11,176	11,217	11,432	12,185	13,510
Secondary	10,635	10,688	11,108	18,996	23,114	19,407
Exports	27,831	55,493	27,641	60,927	68,502	20,934
Imports for consumption	117,600	127,000	123,000	119,000	129,000	163,000
Consumption	109,976	118,515	118,677	124,478	146,920	172,084
Stocks December 31: Consumer	15,357	18,298	13,450	17,191	17,076	13,749
Price, ¢/lb	74	74-81-1/4	81-1/4-79	79	79	79-77-3/4
World						
Production	302,800	398,000	394,000	389,000	423,000	472,000

Secondary Sources. Since secondary sources are closely allied with consumption of new and old nickel scrap, they will be discussed in that category immediately after discussion of refining of nickel.

Recovery Methods(C-6 - C-9)

The metallurgy of nickel can be illustrated with two ores, nickeliferous sulfide and nickeliferous lateritic ores, containing cobalt and varying amounts of iron and gangue. Chemical processing in a typical nickel refinery is shown in the accompanying diagram.

In the case of sulfides, a minor amount of higher-grade ore is smelted directly into blast furnaces. With lower-grade ores, froth flotation may be required for a preliminary concentration of nickel. International Nickel Company employs selective flotation and magnetic separation to divide the bulk concentrate into nickel-, copper-, and iron-rich fractions for separate treatment. The nickel concentrate is treated by pyrometallurgical processes. The hot calcine, plus flux, is smelted in coal-fired reverberatory furnaces operating at about 2200 F. Other procedures also can be used.

The product of these operations, termed furnace matte, is cast into 25-ton molds, in which it is slowly cooled to form large, discrete crystals of copper sulfide, nickel sulfide, and precious metals. After crushing and grinding, the metallics are removed magnetically, and the main sulfide fraction is separated into copper and nickel sulfides by froth flotation. A portion of the nickel sulfide is sintered to granular nickel oxide and marketed directly for alloy-steel production.

Two major processes are employed to convert nickel sulfide to pure metal for market. One involves electrolytic refining to give nickel, cobalt, and precious metals. The nickel sulfide from slowly cooled matte is melted, cast directly into sulfide anodes, and electrolytically refined to nickel cathodes, with concurrent recovery of elemental sulfur, cobalt, selenium, and precious metals.

The other major process, the Mond nickel carbonyl process, is used in Great Britain to produce refined nickel from nickel oxide sinter. The sulfide is ground, calcined, reduced with water gas, and treated with carbon monoxide to volatilize nickel as nickel carbonyl, which is decomposed at 400 F to yield high-purity nickel in pellet form. Copper and cobalt salts and precious metals are recovered from the residue.

In a modification of this process, the matte is ground, roasted to oxide, and leached with dilute sulfuric acid to remove copper, which is recovered electrolytically from the leach solution. The nickel-bearing residue also is recovered electrolytically. Nickel and copper also can be separated by a pressure hydrometallurgical process. A suspension of finely ground nickel concentrate is leached with ammoniacal solution with vigorous aeration. The metal sulfides are oxidized to sulfates, the iron hydrolyzes and precipitates into the residue. Copper and trace metals are separated from the filtrate and the ammoniacal nickel-cobalt solution is hydrogenated under pressure to yield a nickel powder and a nickel-cobalt residue. Ammonium sulfate is a by-product of this operation.

The lateritic ores contain about 1.5 to 3 percent nickel and practically no copper. The richer ores are blast-furnace smelted with coke and gypsum to produce nickel matte for converting and subsequent refining. Ore can also be smelted to ferronickel in an electric furnace. Combined pyro- and hydrometallurgical techniques have been employed in which nickel is precipitated as basic nickel carbonate and then calcined to an oxide powder. Nickel and cobalt may be selectively dissolved by pressure under sulfuric acid leaching; after iron removal, they are precipitated with hydrogen sulfide. The slurry of sulfides then is upgraded to the metals by a hydrometallurgical process.

Figure C-1 is a flow diagram of the steps (many of them chemical) employed at the Sherritt Gordon Nickel Refinery, Fort Saskatchewan, Canada, to process nickel concentrate.

Use Pattern(C-7)

Nickel consumption in 1965 in the free world rose to an estimated 730,000,000 lb compared with 670,000,000 lb in 1964.

Stainless steels accounted for nearly 250,000,000 lb of the total nickel consumed. The plating industry was second, accounting for 110,000,000 lbs. High-nickel alloys ranked third with approximately 100,000,000 lb. These alloys made the greatest

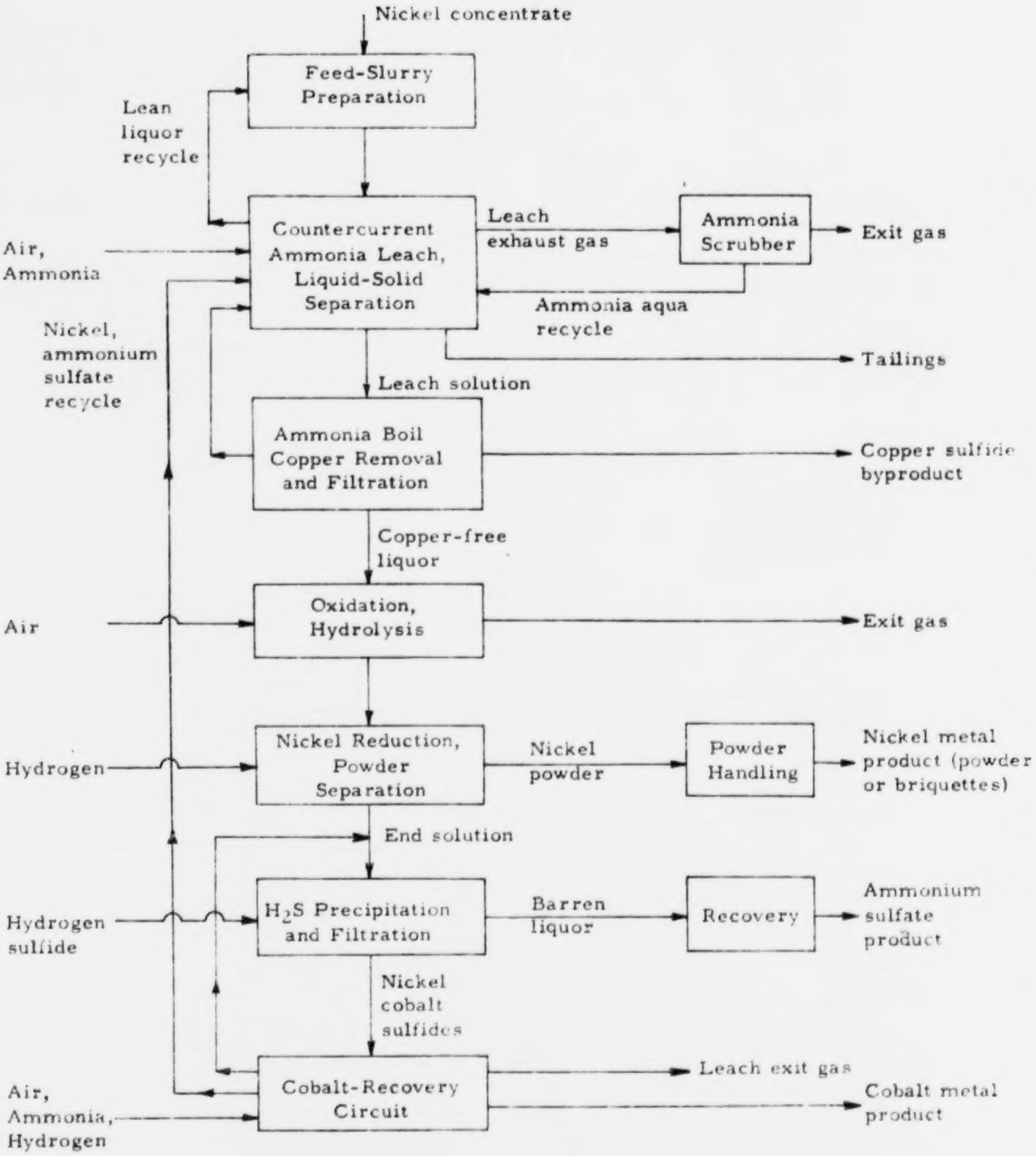

FIGURE C-1. PROCESSING STEPS FOR NICKEL AT SHERRITT GORDON NICKEL REFINERY, FORT SASKATCHEWAN, CANADA advance in consumption, attributable mainly to their increased use in the chemical, marine, electronic, nuclear power, and aerospace fields.

Tables C-3, C-4, and C-5 show the consumption in the United States of new and old nickel scrap and of nickel exclusive of scrap. Of primary interest in connection with this study are the data given in Table C-5 on consumption in the United States of nickel exclusive of scrap according to use. These data show that, with the exception of a slight decrease in ceramics, nickel consumption in the United States increased in all categories reported. Comparatively large gains were achieved in ferrous stainless steels, nonferrous alloys, and in the "other" category, which includes the chemical uses. Fields of consumption are discussed below.

TABLE C-3. STOCKS AND CONSUMPTION OF NEW AND OLD NICKEL SCRAP IN THE UNITED STATES IN 1965

Gross Weight in Short Tons

Class of Consumer and Type of Scrap	Stocks at Beginning of Year	Receipts	Consumption			Stocks at End of Year
			New	Old	Total	
			Smelters and Refiners			
Unalloyed nickel	184	1,079	696	388	1,084	179
Monel metal	404	2,177	507	1,482	1,989	592
Nickel silver[a]	838	4,758	500	4,342	4,842	754
Miscellaneous nickel alloys	7	5,437	1	5,436	5,437	7
Nickel residues	80	233	--	245	245	68
Total	675	8,926	1,204	7,551	8,755	846
			Foundries and Plants of Other Manufacturers			
Unalloyed nickel	8,114	6,772	1,669	7,985	9,654	5,232
Monel metal	111	534	77	496	573	72
Nickel silver[a]	4,179	13,359	13,391	117	13,508	4,030
Miscellaneous nickel alloys	81	99	24	150	174	6
Nickel residues	513	1,959	1,897	80	1,977	495
Total	8,819	9,364	3,667	8,711	12,378	5,805
			Grand Total			
Unalloyed nickel	8,298	7,851	2,365	8,373	10,738	5,411
Monel metal	515	2,711	584	1,978	2,562	664
Nickel silver[a]	5,017	18,117	13,891	4,459	18,350	4,784
Miscellaneous nickel alloys	88	5,536	25	5,586	5,611	13
Nickel residues	593	2,192	1,897	325	2,222	563
Total	9,494	18,290	4,871	16,262	21,133	6,651

(a) Excluded from totals because it is copper-base scrap, although containing substantial nickel.

TABLE C-4. NICKEL (EXCLUSIVE OF SCRAP) CONSUMED IN THE UNITED STATES ACCORDING TO FORM

Short Tons

Form	1956-60 (Average)	1961	1962	1963	1964	1965
Metal	85,617	101,394	103,485	110,365	123,443	146,357
Oxide powder and oxide sinter	18,180	15,883	13,760	12,461	21,090	23,047
Matte	4,829	16	3	2	2	3
Salts[(a)]	1,350	1,222	1,429	1,650	2,385	2,677
Total	109,976	118,515	118,677	124,478	146,920	172,084

(a) Figures do not cover all consumers.

TABLE C-5. NICKEL (EXCLUSIVE OF SCRAP) CONSUMED IN THE UNITED STATES ACCORDING TO USE

Short Tons

Use	1956-60 (Average)	1961	1962	1963	1964	1965
Ferrous						
Stainless steels	29,049	34,213	29,711	34,140	48,301	51,700
Other steels	16,296	18,238	18,608	19,727	24,679	27,009
Cast irons	4,933	4,649	5,503	5,901	6,605	6,937
Nonferrous[(a)]	27,902	28,789	28,215	24,794	23,639	37,082
High-temperature and electrical resistance alloys	9,852	11,294	12,862	13,505	15,291	18,464
Electroplating						
Anodes[(b)]	15,498	15,737	16,953	18,621	19,446	19,450
Solutions[(c)]	958	770	904	1,050	1,645	2,037
Catalysts	1,707	1,519	1,566	1,613	2,167	2,241
Ceramics	375	366	439	554	529	501
Magnets	855	773	910	777	664	828
Other	2,551	2,167	3,006	3,796	3,954	5,835
Total	109,976	118,515	118,677	124,478	146,920	172,084

(a) Comprises copper-nickel alloys, nickel silver, brass, bronze, beryllium alloys, magnesium and aluminum alloys, Monel, Inconel, and malleable nickel.

(b) Figures represent quantity of nickel used for production of anodes, plus cathodes used as anodes in plating operations.

(c) Figures do not cover all consumers.

Alloys.(C-10 – C-13) For the year 1965, approximately 141,000 tons of nickel were used in the production of ferrous alloys, nonferrous alloys, and high-temperature and electrical-resistance alloys. This total includes wrought and cast alloys. Wrought alloy steels are designated as SAI and AISI series 2300, 2500, 3100, 3300, 4300, 4600, 4800, 8600, 9300, 9400, 9700, and 9800. They usually contain chromium, or chromium and molybdenum, in addition to nickel. Cast-steel alloys are improved by nickel. Various types of cast products contain nickel, nickel-vanadium, nickel-manganese, nickel-molybdenum, nickel-chromium, and nickel-chromium-molybdenum. Alloy cast irons usually contain one or more of chromium, manganese, copper, and silicon; nickel improves their machinability. Clad steels are composite products protected on one or both sides with a bonded layer of nickel, a high-nickel alloy, or a stainless steel. Thermal-expansion alloys of the nickel-iron type contain small percentages of chromium, manganese, silicon, tungsten, molybdenum, copper, cobalt, and titanium. These are used in fabricated shapes for metal-to-glass seals. High-copper, low-nickel alloys of appropriate compositions show little or no change in electrical resistance with change in temperature. They are employed in instruments and controls where constancy of resistance is required. Cupro-nickels have good strength and resistance to corrosion in salt water and are used chiefly for condenser tubes and salt-water piping. Coinage alloys of copper and nickel, often with zinc and tin, were among the earliest alloy compositions known to man, and are used widely. It is estimated that 150 million pounds of nickel have been used internationally in coinage during the last 75 years. Electrical-resistance alloys are important components of rheostats, shunts, and thermocouples. Aluminum-nickel alloys are used in the aviation and automotive fields. Nickel silvers are used in household items, plumbing fixtures, and jewelry. The nickel brasses and nickel bronzes find applications in bearings, valves, and pumps. Stainless steels find many uses, including uses in chemical, petroleum, and food-processing equipment.

An alloy containing 98 percent nickel and 2 percent thorium oxide has been developed for equipment that operates at temperatures from 1800 to 2400 F. This alloy is obtained by a technique that produces uniform dispersions of millimicron-size particles of stable oxides of thorium, aluminum, zirconium, and titanium within the grain structure of base metals and some of their alloys, including copper, lead, silver, iron, molybdenum, and tungsten, in addition to nickel. Nickel, its important alloys, and their uses are outlined in Table C-6.

Because of the excellent corrosion resistance of nickel and high-nickel alloys, e.g., Monel, Inconel, 18-8 SS (Types 302 and 304) and 18-8 Mo SS (Type 316), these are used widely in food-processing equipment. The following is a list of such processes and their products:

Refrigerating brines
Pickling brines
Seafood processing
Sugar refining
    Cane sugar and molasses
    Beet sugar and Steffens filtrate
    Corn starch
    Corn sugar and syrup
Pectin
Fruit joices and syrups
Carbonated water and beverages

TABLE C-6. NICKEL, ITS IMPORTANT ALLOYS, AND THEIR USES

Principal Elements	Approximate Nickel Content, percent	Alloy	Use
Nickel	99.4	Commercially pure wrought nickel	Corrosion resistance; thermal conductivity; radio and electronic tube parts; magnetostriction oscillators; coinage
	90-99.5	Anodes	Plating
Nickel and iron	0.5-9	Wrought-alloy steels	Transportation and earth-moving equipment; heavy machinery; low-temperature applications
	0.5-5	Cast alloy steels	Heavy machinery; railroad; steel mill rolls
	1-6 and 14-36	Alloy cast irons	Heavy machinery; machine tools; automotive and diesel engines; brake drums; corrosion resistance; abrasion resistance
	30-90	Magnetic alloys	Communications; electrical equipment
	14-28	Permanent-magnet alloys	Motor, generator, radio, and instrument parts
	8-27	Nonmagnetic alloys	Electrical and magnetic equipment parts
	5-40	Clad steels	Petroleum, chemical, and food-processing equipment
	22-50	Thermal-expansion alloys	Chronometer springs; radio; tuning forks; thermostats
Nickel and copper	2-13	High-copper alloys	Instrument and control parts
	10-30	Cupronickels	Tubes and plates in condensers and heat exchangers
	25	Coinage alloy	Coinage
	45	Electrical-resistance alloy	Resistance elements; thermocouples
	Over 50	High-nickel alloys	Corrosion resistance; strength; chemical, petroleum, and food-processing equipment
Nickel and chromium	80	Electrical-resistance alloys	Heating elements
	2-73	Special heat-resisting alloys	Gas turbine and jet engine parts
Nickel and aluminum	2	Cylinder head and piston alloys	Automotive and aircraft parts
	1-2.5	Low-expansion alloys	Automotive and aircraft parts
	1	Bearing alloys	Automotive and aircraft parts
Nickel, copper, and zinc	5-30	Nickel silvers	Flat-ware; hollow-ware; electrical equipment; telephone equipment; jewelry; zippers; plumbing fixtures; architectural trim
Nickel, copper, and tin	1-15	Nickel brasses and bronzes	Spring applications; bearings; valves; pumps
Nickel, chromium, and iron	6-20	Stainless steels	Corrosion resistance; strength; chemical, petroleum, and food-processing equipment
	4-85	Heat-resisting alloys	High-temperature applications
	35-60	Electrical-resistance alloys	Heating elements
Others	0.5-98	Age-hardenable alloys	Corrosion resistance; strength; special equipment
	94-98	Nickel-manganese alloys	Spark plugs; ignition tubes
	55-65	Nickel-molybdenum-iron and nickel-molybdenum-chromium-iron alloys	Corrosion resistance; strength; special equipment
	85	Nickel-silicon alloys	Corrosion resistance; strength; special equipment

Gelatin
Condiments
Glutamic acid and monosodium glutamate
Mayonnaise and salad dressing
Vinegar
Vanilla extract
Tartaric acid
Breakfast cereals
Manufacture and washing of sausage casing
Meat-joice extract
Oleomargarine and butter
Maraschino cherries
Baker's yeast
Flour bleaching
Coffee brew and extract
Pea canning
Corn canning
Tomato processing.

No attempt will be made to present all the corrosion data in connection with the above food processes. For this, the references should be consulted. However, the data given in Table C-7 on hot processing of maraschino cherries is typical.

TABLE C-7. PLANT CORROSION TESTS IN HOT PROCESSING OF MARASCHINO CHERRIES

Conditions of Test: In syruping tank with cherry liquor containing 600-1000 ppm of SO_2 at start. Temperature 132 to 160 F. Duration of test, 183 days, during which 25 batches were processed, each requiring about 4 days. Balance of time specimens were exposed to air at room temperature. No aeration or agitation reported.

Material	Indicated Corrosion Rate, inch penetration per year
Monel	0.0003
Nickel	0.0025
Inconel	0.0001
18-8 SS (Type 302)	<0.0001
18-8 SS (Type 304)	<0.0001
18-8 Mo SS (Type 316)	0.0001

Manufacturers/distributors of nickel and nickel alloys include:

Allied Chemical Corporation, General Chemical Division
Atlantic Equipment Engineers
Atomergic Chemmetals
Belmont Smelting and Refining Works
J. T. Baker Chemical Company
Bram Metallurgical Chemical
Cerac Incorporated
Consolidated Astronautics
Du Pont Pigments Department
Harshaw Chemicals
International Nickel
Materials Research
MHD Research, Incorporated
McGean Chemical
3 M Company
National Research Corporation
Octagon Process
Charles Pfizer, Minerals, Pigments, and Metals
Reading Alloys
Titanium Alloy
Union Carbide Metals
United Minerals and Chemicals
Var-Lac-Oid Company
Ventron Corporation
Vitro Labs.

Electroplating.(C-14) Anodes. The 1965 data indicate that 19,450 tons of nickel were consumed in anodes in electroplating. Very likely this is a conservative figure.

The manufacturers/distributors of anodes include:

American Smelting and Refining
Atlantic Equipment Engineers
Cerac, Incorporated
Consolidated Astronautics
Falconbridge Nickel Mines, Limited
Girdler
Hanson-Van Winkle-Munning Company
Harshaw
International Nickel
McGean
Mallinckrodt
Reading Alloys
Sherritt Gordon Mines, Limited
Udylite
Ventron, Incorporated.

Electrolytic Chemicals.(C-15, C-16) The 1965 data showing that 2037 tons of nickel were used in electroplating solutions also seem conservative. For example, it has been estimated that 12,000 tons of nickel sulfate (presumably the heptahydrate) were used in electroplating during 1965. This alone would account for about 2500 tons of nickel. Also during the same period, 1,500 tons of nickel chloride were consumed – the equivalent of 370 tons of nickel. In the so-called electroless nickel-plating process, nickel chloride and sulfate are the chief sources of nickel. In addition, 60 tons of basic nickel carbonate and 75 tons of nickel acetate were consumed. Nickel fluoborate and nickel sulfamate consumptions were small. Nickel sulfamate is generally prepared "in situ" from basic nickel carbonate and sulfamic acid, and actual figures on captive use and production are not available. Finally, small quantities of nickel additives, e.g., brighteners, are used in electroplating.

Manufacturers/distributors of important salts used in electroplating include:

Nickel Acetate

Allied Chemical, General Chemical Division
Atomergic Chemetals
J. T. Baker Chemical
Copper Pigment & Chemical Works
Fielding Chemical
Hall Chemical
Harshaw Chemical
McGean Chemical
McKesson & Robbins (Distributor)
Shepherd Chemical
VAR-LAC-OID Chemical

Nickel Carbonate, Basic

Allied Chemical, General Chemical Division
Atomergic Chemetals
Ceramic Color & Chemical Manufacturing
Hall Chemical
Harshaw Chemical
M&T Chemicals
McGean Chemical
Nuodex Division
Octagon Process
Shepherd Chemical
VAR-LAC-OID Chemical

Nickel Chloride

Alfa Inorganics
Allied Chemical, B & A Products
Atomergic Chemetals
J. T. Baker Chemical
Ceramic Color & Chemical Manufacturing
Copper Pigment & Chemical Works
Fielding Chemical
Harshaw Chemical
Harstan Chemical
MRC Corporation
Mallinckrodt Chemical Works
McGean Chemical
McKesson & Robbins (Distributor)
Nuodex Division
Octagon Process
Pearsall Chemical
Seaway Chemical (Distributor)
Southern California Chemical
Tar Residuals (Distributor)
Thompson-Hayward Chemical (Distributor)
United Mineral & Chemical
VAR-LAC-OID Chemical

Nickel Hydroxide (ic)

Atomergic Chemetals
McGean Chemical
VAR-LAC-OID Chemical

Nickel Hydroxide (ous)

[illegible] Chemical
Atomergic Chemetals
Ceramic Color & Chemical Manufacturing
Hall Chemical
McGean Chemical
Shepherd Chemical
Southern California Chemical

Nickel Sulfamate

Atomergic Chemetals
City Chemical Corporation
Copper Pigment & Chemical Works
Fielding Chemical
Harshaw Chemical
Harstan Chemical
MRC Corporation
M&T Chemicals
McKesson & Robbins (Distributor)
Reinhard Chemicals
VAR-LAC-OID Chemical

Nickel Sulfate (Single)

Allied Chemical, B & A Products
American Smelting & Refining
Atomergic Chemetals
J. T. Baker Chemical
Browning Chemical (Distributor)
Cerac, Inc.
Ceramic Color & Chemical Manufacturing
Copper Pigment & Chemical Works
Davison Chemical Division (Distributor)
Electronic Space Products
Faesy & Besthoff (Distributor)
Fielding Chemical
Fisher Scientific
Harshaw Chemical
Harstan Chemical
MRC Corporation
M&T Chemicals
Mallinckrodt Chemical Works
McGean Chemical
McKesson & Robbins (Distributor)
Nuodex Division
Octagon Process
Pearsall Chemical
Phelps Dodge Refining
Seaway Chemical (Distributor)
Shepherd Chemical
Southern California Chemical
Sylvan Chemical
Tar Residuals (Distributor)
Thompson-Hayward Chemical (Distributor)
United Mineral & Chemical

Nickel Ammonium Sulfate (Nickel Salts, Double; Ammonium Nickel Sulfate)

Allied Chemical, General Chemical Division
J. T. Baker Chemical
Copper Pigment & Chemical Works
Electronic Space Products
M&T Chemicals
Mallinckrodt Chemical Works
McGean Chemical
McKesson & Robbins (Distributor)
Octagon Process
Shepherd Chemical

Catalysts.(C-17 – C-22) About 2,200 tons of nickel (exclusive of scrap) were used in 1965 in the manufacture of catalysts. Nickel catalyst in various forms, as indicated in Table C-8, is used primarily in the chemical industry for manufacture of synthesis gas hydrogen and ammonia, hydrogenation, and dehydrogenation.

TABLE C-8. USE OF NICKEL AS A CATALYST BY THE CHEMICAL INDUSTRY

Operation	Process	Catalyst	Annual Market (Estimated)
Hydrogen and ammonia	Reforming, shift conversion, etc.	Supported nickel, iron, etc.	7 to 7.5 million lb; $3.8 to 4.5 million
Hydrogenation	Fat hydrogenation	Nickel (25%) in oil	5.2 million lb; $4 million in United States; 9.2 million lb, $7.15 million in the world
	Selective hydrogenation (in olefin production)	Nickel-chrome on alumina-silica	$1.5 to 2 million
		Supported palladium	
	Cyclohexane-from-benzene	Nickel or platinum	250,000 to 500,000 lb/yr
	Olefin saturation (in pretreating feed to steam-reforming)	Nickel or cobalt-molybdenum	80,000 lb; $60,000-70,000
Dehydrogenation	Butadiene (from butane)	Chrome-alumina	2.5 million lb; $1.5 million
	Butadiene (from butylene)	Calcium-nickel-phosphate	2.2 million lb; $2.75-3 million
	Butadiene (from butylene)	Promoted iron oxide)	
	Styrene (from ethylbenzene)	Promoted iron oxide	1.6 million lb; $600,000

A number of catalyst-consuming interrelated steps are involved in the manufacture of synthesis gas, hydrogen, and ammonia. Nickel deposited on a refractory material is used for reforming in the initial (desulfurization) step. Girdler, Catalyst Chemicals, Incorporated (CCI), and American Cyanamid supply the reforming catalyst. CCI's products are 23 to 35 percent nickel oxide on a refractory material. In service, the nickel oxide is reduced to elemental form. Girdler's standard catalyst is a nickel oxide on a refractory material.

If hydrogen or ammonia is desired after methanation, nickel on a refractory support, largely alumina, is used. CCI, Girdler, and Harshaw offer catalysts for this purpose.

The broad area of hydrogenation is believed to consume about 2,000 tons/yr of nickel in catalysts applications. This includes only fresh nickel, however, and significant quantities of recovered nickel also are used as catalysts.

Raney nickel is the catalyst for hydrogenation of fats, and about 1 million lb/yr are used. "Wet reduced" or "dry reduced" nickel catalysts, which are nickel formate and nickel carbonate respectively, are also used for fat hydrogenation. Whatever the process, the nickel content of fat hydrogenation catalysts is usually 25 percent. Drew, Girdler, and Harshaw account for much of the merchant market. The big captive producers are Lever Brothers, Procter and Gamble, and National Dairy Products Corporation.

Cyclohexane is generally made by hydrogenation of benzene in which both nickel and platinum catalysts are used. Girdler, CCI, UOP, and Harshaw sell nickel catalysts for the job. The total benzene-hydrogenation catalyst market is 250,000 to 500,000 lb/yr, about equally divided between nickel and platinum.

Hydrotreating catalysts were used initially to remove primarily sulfur from petroleum feed stock. Now their purpose is to remove both nitrogen and sulfur compounds. Catalysts are cobalt molybdate or nickel molybdate on alumina with or without silica. Nickel oxide content runs about 2 to 6 percent. It is estimated that about 2 million lb/yr of nickel molybdate catalyst are consumed in hydrotreating.

In the steam-reforming process for treating hydrocarbons, the predominant feed in the U. S. has been natural gas. Since the presence of any unsaturated hydrocarbons causes polymerization and coke formation, it is necessary to saturate them in a pretreatment. For hydrogenation of sulfur-free streams, Girdler and CCI offer nickel catalysts. This market might require 300,000 lb of catalyst, with roughly 80,000 lb of this being replacement.

Estimated United States capacity for dehydrogenating butylenes to butadiene is 665,000 tons/yr. Dow's Type B catalyst, a calcium-nickel phosphate, accounts for about 90 percent of this tonnage and about 2.2 million lb of catalyst.

Manufacturers/distributors of catalysts, including nickel, for desulfurization, hydrogenation, and dehydrogenation are given below:

Catalysts, Desulfurization

American Cyanamid
Catalysts & Chemicals
Chemetron Chemicals
Consolidated Astronautics
Davison Chemical Division
Girdler Catalysts
R. W. Greeff & Company (Distributor)
Harshaw Chemical
Nalco Chemical
Union Carbide, Carbon Products Division

Catalysts, Hydrogenation

American Cyanamid
BASF Colors & Chemicals (Distributor)
J. Bishop Platinum Works
Calsicat Division
Catalysts & Chemicals
Chemetron Chemicals
Consolidated Astronautics
Davison Chemical Division
Dow Chemical
Drew Chemical
Engelhard Industries
Girdler Catalysts
Harshaw Chemical
Hoeganaes Sponge Iron
Mallinckrodt Chemical Works
McGean Chemical
Metallurgical International
Nalco Chemical
Nuodex Division
Procter & Gamble
Shell Chemical
Joseph Turner & Company
Union Carbide, Carbon Products Division
Union Carbide, Linde Division
Von Bree, Incorporated

Catalysts, Dehydrogenation

American Cyanamid
BASF Colors & Chemicals (Distributor)
Calsicat Division
Catalysts & Chemicals
Chemetron Chemicals
Consolidated Astronautics
Davison Chemical Division
Dow Chemical
Engelhard Industries
Girdler Catalysts
Harshaw Chemical
Mallinckrodt Chemical Works
Nalco Chemical
J. A. Samuel & Company
Shell Chemical
Union Carbide, Linde Division

Nickel carbonyl, one of the most toxic nickel compounds, is used as a catalyst in carbonylation reactions, as well as for the preparation of metallic nickel. It is a colorless liquid, insoluble in water, and unreactive with aqueous acids and alkalies, but soluble in organic liquids. Its pertinent physical and chemical properties are:

Vapor pressure (25 C)	580 mm Hg
Specific gravity (25 C)	1.31
Melting point	-25 C
Boiling point	43.2 C
Initial decomposition temperature	50 C.

Nickel carbonyl is prepared by the reaction of carbon monoxide with finely reduced nickel. The latter is obtained by hydrogenation of nickel ores, often in the presence of a catalyst. The decomposition of nickel carbonyl gives high-purity metal for the manufacture of nickel, nickel alloys, nickel catalysts, nickel electrodes, and acrylic esters. In the manufacturing process generally used, the nickel carbonyl is handled entirely as a vapor in a closed system at atmospheric or superatmospheric pressures. Thus, it is not difficult to avoid accidental exposure.

The synthesis of acrylic esters involves reaction of acetylene, carbon monoxide, and an alcohol in presence of nickel carbonyl catalyst. In this manner, a major portion of the total carbon monoxide used may be carbon monoxide gas, the remainder being in the form of nickel carbonyl. The "spent" nickel carbonyl is recovered as nickel chloride in the recycle stream from the synthesis of the acrylate. A small amount of new solution of nickel salt is added to make up for the mechanical and chemical losses in the process. The used catalyst is dissolved in sodium hydroxide and resulting nickel in the hydroxide is converted in contact with carbon monoxide at high pressure to nickel carbonyl. The temperature is maintained above 100 C and the nickel carbonyl leaves the reactor with an excess of carbon monoxide. The nickel carbonyl is stored in this manner. Excess carbon monoxide is recycled through the process. Inert gases such as argon, nitrogen, and methane, which accumulate in the gas stream, must be vented to maintain the partial pressure of carbon monoxide above 1,500 psi. The liquid slurry from the reaction is discarded after being treated to remove all of the nickel carbonyl. The waste-gas streams are passed through a decontamination furnace to destroy nickel carbonyl. This venting provides the major loss of nickel carbonyl, but in spite of this, the yield of carbonyl based on nickel is high.

Rohm and Haas, and Dow Badische manufacture acrylics/acrylates using the acetylene process and nickel carbonyl as a catalyst. The capacity of Rohm and Haas' plant at Deer Park, Texas, is 80 million pounds. Dow Badische's plant at Freeport, Texas, has a capacity of 15 million pounds. Assuming a pound loss of catalyst for each ton of acrylic/acrylate produced, 47,500 pounds of nickel carbonyl per year might be consumed in the process. This might be a potential source of contamination.

Within the broad category of organic synthesis are numerous catalytic reactions; however, none of these employ nickel catalysts on a commercial scale.

Below is a list of manufacturers/distributors of nickel and nickel compounds used in the preparation of nickel catalysts.

Nickel Acetate

Allied Chemical, General
 Chemical Division
Atomergic Chemetals
J. T. Baker Chemical
Copper Pigment &
 Chemical Works
Fielding Chemical
Hall Chemical
Harshaw Chemical
McGean Chemical
McKesson & Robbins
 (Distributor)
Shepherd Chemical
Var-Lac-Oid Chemical

Nickel Ammonium Sulfate (Nickel Salts, Double; Ammonium Nickel Sulfate)

Allied Chemical, General
 Chemical Division
J. T. Baker Chemical
Copper Pigment &
 Chemical Works
Electronic Space Products
M& T Chemicals
Mallinckrodt Chemical
 Works
McGean Chemical
McKesson & Robbins
 (Distributor)
Octagon Process
Shepherd Chemical

Nickel Benzenesulfonate

City Chemical Corporation

Nickel Black (See Nickel Oxide (ic)

Nickel Bromide

ALFA Inorganics
Atomergic Chemetals
City Chemical Corporation
Cooper Chemical
Copper Pigment &
 Chemical Works
Fielding Chemical
Harstan Chemical
McKesson & Robbins
 (Distributor)
Research Inorganic Chemicals
Rocky Mountain Research
Shepherd Chemical
Var-Lac-Oid Chemical

Nickel Carbonate, Basic

Allied Chemical, General
 Chemical Division
Atomergic Chemetals
Ceramic Color &
 Chemical Manufacturing
Hall Chemical
Harshaw Chemical
M&T Chemicals
McGean Chemical
Nuodex Division
Octagon Process
Shepherd Chemical
Var-Lac-Oid Chemical

Nickel, Carbonyl

J. T. Baker

Nickel Chloride

ALFA Inorganics
Allied Chemical, B & A
 Products
Atomergic Chemetals
J. T. Baker Chemical
Ceramic Color & Chemical
 Manufacturing
Fielding Chemical
Harshaw Chemical
Harstan Chemical
MRC Corporation
Mallinckrodt Chemical
 Works
McGean Chemical

Nickel Chloride (Continued)

Copper Pigment &
 Chemical Works
Nuodex Division
Octagon Process
Pearsall Chemical
Seaway Chemical
 (Distributor)
Southern California
 Chemical
McKesson & Robbins
 (Distributor)
Tar Residuals (Distributor)
Thompson-Hayward Chemical
 (Distributor)
United Mineral & Chemical
Var-Lac-Oid Chemical

Nickel Chromate

Atomergic Chemetals
City Chemical Corporation
Var-Lac-Oid Chemical

Nickel Cyanide

Aceto Chemical
Atomergic Chemetals
City Chemical Corporation
Copper Pigment &
 Chemical Works
Octagon Process
Special Chemicals
Var-Lac-Oid Chemical

Nickel Dimethylglyoxime

City Chemical Corporation
Premium Chemical Corporation

Nickel Fluoborate

ALFA Inorganics
Allied Chemical, General
 Chemical Division
Atomergic Chemetals
Harshaw Chemical
Harstan Chemical
M&T Chemicals
McKesson & Robbins (Distributor)
Var-Lac-Oid Chemical

Nickel Fluoride

Allied Chemical, General
 Chemical Division
Atomergic Chemetals
Electronic Space Products
Harshaw Chemical
Ozark-Mahoning
Peninsular Chemresearch
Var-Lac-Oid Chemical

Nickel Formate

Aceto Chemical (Distributor)
Atomergic Chemetals
Cooper Chemical
Cooper Pigment & Chemical
 Works
Harshaw Chemical
McGean Chemical
Nuodex Division
Octagon Process
Shepherd Chemical
Var-Lac-Oid Chemical

Nickel Hydrate see Nickel Hydroxide (ous)

Nickel Hydroxide (ic)

Atomergic Chemetals
McGean Chemical
Var-Lac-Oid Chemical

Nickel Hydroxide (ous)

Aceto Chemical
Atomergic Chemetals
Ceramic Color & Chemical Manufacturing
Hall Chemical
McGean Chemical
Shepherd Chemical
Southern California Chemical

Nickel Iodide

Atlantic Equipment Engineers
Atomergic Chemetals
City Chemical Corporation
Cooper Chemical
Deepwater Chemical
Fielding Chemical
Research Inorganic Chemical
Rocky Mountain Research
Var-Lac-Oid Chemical

Nickel Metal

Allied Chemical, General Chemical Division
Atlantic Equipment Engineers
Atomergic Chemetals
Belmont Smelting & Refining Works
Bram Metallurgical-Chemical
Cerac, Inc.
Consolidated Astronautics
Harshaw Chemical
International Nickel
Materials Research
McGean Chemical (Distributor)
Octagon Process
Chas. Pfizer, Minerals, Pigments & Metals
United Mineral & Chemical
Var-Lac-Oid Chemical

Raney Nickel

Gelman Paint & Varnish

Magnets.(C-24, C-25, C-26) The 1965 data indicate that 828 tons of nickel were used in the production of magnets, and presumably magnetic materials. Generally, magnetic alloys have high permeabilities at small field strengths. One of the best is Permalloy (78.5 percent nickel and 21.5 percent iron). Hipernik (50 percent nickel and 50 percent iron) has high saturation values and is useful for transformers; its magnetic properties are less sensitive to heat treatment than Permalloy Modifications of the two base compositions including Supermalloy, Mumetal and Perminvar.

Permanent magnetic alloys contain cobalt and aluminum and sometimes copper and titanium in addition to nickel. The Alnico alloys are precipitation hardened. Cunife and Cunico are two widely used nickel-containing magnetic ductile alloys. A nickel-iron alloy, Satmumetal, with high saturation flux, density, and permeability has been developed for use in transformers, Hall effect multipliers, and other components controlled by direct magnetic fields.

Ceramics.(C-27, C-28) About 500 tons of nickel were consumed in the ceramics industry during 1965. Specific areas of use are:

Nickel aluminate is a spinel with a melting point about 2000 F that is useful as a high temperature structural material.

Nickel-bonded titanium carbide is the most commonly used of the so-called cement materials for high-temperature structural applications, e.g., turbine blading, tool bits, and bearing and seal material.

Nickel boride and nickel nitride are both used in high temperature applications.

Nickel oxide in ferromagnetic ferrites is one of the primary constituents, along with iron oxide and zinc oxide. The quantity may vary from 3 to 25 percent. Nickel oxides and carbonate are desirable for ferrite application. Nickelous oxide and nickelic oxide are useful as colorants in ceramics. Nickel oxide is sometimes used to decolorize potash glass. Nickel silicate may be used for the same purpose. The use of nickel oxide in porcelain enamel compositions is usually confined to the ground coat, in which it is used with cobalt, or cobalt and manganese. Nickel oxide is also used in cover coat enamels to produce a daylight shade for reflector units. Nickelous oxide is used in glazes to produce blues, grays, browns, and yellows. Nickel salts, especially nickelous oxide, have long been used in the porcelain enameling industry as a flashing on the part after pickling and prior to application of porcelain enamel. Nickelous stannate has been suggested for use in barium titanate capacitors. Nickel sulfate solutions are consumed in the enameling industry as a "nickel bath" following the acid rinse in the pickle operation. The nickel is deposited on the metal surface by electromotive displacement and, if properly controlled, aids in improving ground coat adherence over a wide firing range. Usually nickel is a necessity when processing cold rolled stock and is an important factor when applying cover coats directly on special steels.

Other Uses. (C-29 - C-34) This category in the use of nickel in 1965 amounted to 5,835 tons or over 11 million pounds. Diverse chemical and general applications are included. Lists of available nickel compounds and manufacturers/distributors of nickel compounds are included. Uses for nickel compounds that have not been identified previously in this report are:

(1) Gasoline additives

Nickel isodecylorthophosphate is a multifunctional gasoline additive manufactured by Sinclair Refining

(2) Fungicides

Nickel sulfate
Nickel acetate
Nickel dibutyldithiocarbamate

(3) Metalworking

Nickel fluoride
Nickel naphthenate
Nickel oleate
Nickel stearate

(4) Metalizing and mordanting (dyes)

Nickel stearate

(5) Office copying equipment

Nickel stearate

(6) Electrodes for fuel cells

Nickel boride

(7) Storage batteries

Nickel hydroxide in alkaline storage batteries
Nickel/nickel oxides in nickel-cadmium batteries

(8) Pigments

Nickel glyoxime

(9) Antioxidant

Nickel dibutyl dithiocarbamate (GRS rubber)

(10) Separation of aromatic hydrocarbons

Nickelous thiocyanate
Nickelous bromide.

Following is a list of manufacturers and distributors of some commercially significant nickel alloys and nickel chemicals.

Nickel Acetate

- Allied Chemical, General Chemical Division
- Atomergic Chemetals
- J. T. Baker Chemical
- Copper Pigment & Chemical Works
- Fielding Chemical
- Hall Chemical
- Harshaw Chemical
- McGean Chemical
- McKesson & Robbins (Distributor)
- Shepherd Chemical
- Var-Lac-Oid Chemical

Nickel Alloys (see also Nickel Titanium)

- Atlantic Equipment Engineers
- Belmont Smelting & Refining Works
- Bram Metallurgical-Chemical
- Consolidated Astronautics
- Du Pont, Pigments Department
- Materials Research
- Chas. Pfizer, Minerals, Pigments & Metals
- Reading Alloys
- 3M Company
- Titanium Alloy
- Ventron Corporation

Nickel Ammonium Sulfate (Nickel Salts, Double; Ammonium Nickel Sulfate)

- Allied Chemical, General Chemical Division
- J. T. Baker Chemical
- Copper Pigment & Chemical Works
- Electronic Space Products
- M&T Chemicals
- Mallinckrodt Chemical Works
- McGean Chemical
- McKesson & Robbins (Distributor)
- Octagon Process
- Shepherd Chemical

Nickel Black see Nickel Oxide (ic)

Nickel Bromide

- ALFA Inorganics
- Atomergic Chemetals
- City Chemical Corporation
- Cooper Chemical
- Copper Pigment & Chemical Works
- Fielding Chemical
- Harstan Chemical
- McKesson & Robbins (Distributor)
- Research Inorganic Chemical
- Rocky Mountain Research
- Shepherd Chemical
- Var-Lac-Oid Chemical

Nickel Carbonate (Basic)

- Allied Chemical, General Chemical Division
- Atomergic Chemetals
- Ceramic Color & Chemical Manufacturing
- Hall Chemical
- Harshaw Chemical
- M&T Chemicals
- McGean Chemical
- Nuodex Division
- Octagon Process
- Shepherd Chemical
- Var-Lac-Oid Chemical

Nickel Chloride

- ALFA Inorganics
- Allied Chemical, B & A Products
- Atomergic Chemetals
- J. T. Baker Chemical
- Ceramic Color & Chemical Manufacturing
- Copper Pigment & Chemical Works
- Fielding Chemical
- Harshaw Chemical
- Harstan Chemical
- MRC Corporation
- Mallinckrodt Chemical Works
- McGean Chemical
- McKesson & Robbins (Distributor)
- Nuodex Division
- Octagon Process
- Pearsall Chemical
- Seaway Chemical (Distributor)
- Southern California Chemical
- Tar Residuals (Distributor)
- Thompson-Hayward Chemical (Distributor)
- United Mineral & Chemical
- Var-Lac-Oid Chemical

Nickel Chromate

- Atomergic Chemetals
- City Chemical Corporation
- Var-Lac-Oid Chemical

Nickel Cyanide

- ACETO Chemical
- Atomergic Chemetals
- City Chemical Corporation
- Copper Pigment & Chemical Works
- Octagon Process
- Special Chemicals
- Var-Lac-Oid Chemical

Nickel Fluoborate

- ALFA Inorganics
- Allied Chemical, General Chemical Division
- Atomergic Chemetals
- Harshaw Chemical
- Harstan Chemical
- M&T Chemicals
- McKesson & Robbins (Distributor)
- Var-Lac-Oid Chemical

Nickel Fluoride

Allied Chemical, General Chemical Division
Atomergic Chemetals
Electronic Space Products
Harshaw Chemical
Ozark-Mahoning
Peninsular Chemresearch
Var-Lac-Oid Chemical

Nickel Formate

ACETO Chemical (Distributor)
Atomergic Chemetals
Cooper Chemical
Copper Pigment & Chemical Works
Harshaw Chemical
McGean Chemical
Nuodex Division
Octagon Process
Shepherd Chemical
Var-Lac-Oid Chemical

Nickel Hydrate see Nickel Hydroxide (ous)

Nickel Hydroxide (ic)

Atomergic Chemetals
McGean Chemical
Var-Lac-Oid Chemical

Nickel Hydroxide (ous)

ACETO Chemical
Atomergic Chemetals
Ceramic Color & Chemical Manufacturing
Hall Chemical
McGean Chemical
Shepherd Chemical
Southern California Chemical

Nickel Iodide

Atlantic Equipment Engineers
Atomergic Chemetals
City Chemical Corporation
Cooper Chemical
Deepwater Chemical
Fielding Chemical
Research Inorganic Chemical
Rocky Mountain Research
Var-Lac-Oid Chemical

Nickel Metal

Allied Chemical, General Chemical Division
Atlantic Equipment Engineers
Atomergic Chemetals
Belmont Smelting & Refining Works
Bram Metallurgical-Chemical
Cerac, Inc.
Consolidated Astronautics
Harshaw Chemical
International Nickel
Materials Research
McGean Chemical (Distributor)
Octagon Process
Chas. Pfizer, Minerals, Pigments & Metals
United Mineral & Chemical
Var-Lac-Oid Chemical

Nickel Naphthenate

Advance Division, Carlisle Chemical Works
Metalead Products
Mooney Chemicals
Nuodex Division
Shepherd Chemical
Troy Chemical

Nickel Nitrate

Allied Chemical, General Chemical Division
Atomergic Chemetals
J. T. Baker Chemical
Copper Pigment & Chemical Works
Fisher Scientific
Hall Chemical
Harshaw Chemical
Mallinckrodt Chemical Works
McGean Chemical
Shepherd Chemical
Var-Lac-Oid Chemical

Nickel Oxalate

ACETO Chemical
Atomergic Chemetals
City Chemical Corporation
Premium Chemicals
Rocky Mountain Research
Shepherd Chemical

Nickel Oxide (ic)

Allied Chemical, General Chemical Division
Atlantic Equipment Engineers
Atomergic Chemetals
J. T. Baker Chemical
McGean Chemical
United Mineral & Chemical
Var-Lac-Oid Chemical

Nickel Oxide (ous) (Nickel Black, Nickel Peroxide, Green Nickel Oxide, Nickel Protoxide)

Atomergic Chemetals
Cerac, Inc.
Ceramic Color & Chemical Manufacturing
Electronic Space Products
Harshaw Chemical

Nickel Perchlorate

Atomergic Chemetals
G. Frederick Smith Chemical

Nickel Peroxide see Nickel Oxide (ic)

Nickel Powder

American Smelting & Refining
Atlantic Equipment Engineers
Atomergic Chemetals
Belmont Smelting & Refining Works
Bram Metallurgical-Chemical
Cerac, Inc.
Consolidated Astronautics
Copper Pigment & Chemical Works
Electronic Space Products
Glidden Company
International Nickel
M&T Chemicals
Metallurgical International
Var-Lac-Oid Chemical

Nickel Protoxide see Nickel Oxide (ous)

Nickel Salts, Double see Nickel Ammonium Sulfate

Nickel Salts, Single see Nickel Sulfate

Nickel Stearate

- Atomergic Chemetals
- R. W. Greeff & Company (Distributor)
- Mathe Chemical
- Mooney Chemicals
- Shepherd Chemical
- WITCO Chemical, Organics Division

Nickel Sulfamate

- Atomergic Chemetals
- City Chemical Corporation
- Copper Pigment & Chemical Works
- Fielding Chemical
- Harshaw Chemical
- Harstan Chemical
- MRC Corporation
- M&T Chemicals
- McKesson & Robbins (Distributor)
- Reinhard Chemicals
- Var-Lac-Oid Chemical

Nickel Sulfate (Nickel Salts, Single)

- Allied Chemical, B & A Products
- American Smelting & Refining
- Atomergic Chemetals
- J. T. Baker Chemical
- Browning Chemical (Distributor)
- Cerac, Inc.
- Ceramic Color & Chemical Manufacturing
- Copper Pigment & Chemical Works
- Davison Chemical Division (Distributor)
- Electronic Space Products
- Faesy & Besthoff (Distributor)
- Fielding Chemical
- Fisher Scientific
- Harshaw Chemical
- Harstan Chemical

Nickel Sulfate (Nickel Salts, Single) (Continued)

- MRC Corporation
- M&T Chemicals
- Mallinckrodt Chemical Works
- McGean Chemical
- McKesson & Robbins (Distributor)
- Nuodex Division
- Octagon Process
- Pearsall Chemical
- Phelps Dodge Refining
- Seaway Chemical (Distributor)
- Shepherd Chemical
- Southern California Chemical
- Sylvan Chemical
- Tar Residuals (Distributor)
- Thompson-Hayward Chemical (Distributor)
- United Mineral & Chemical

Nickel Titanate

- Atlantic Equipment Engineers
- Atomergic Chemetals
- Cerac, Inc.
- Electronic Space Products
- Shepherd Chemical
- Rocky Mountain Research
- Sherwin-Williams
- Titanium Alloy

Nickel Titanium

- Atlantic Equipment Engineers
- Belmont Smelting & Refining Works
- Cerac, Inc.
- Consolidated Astronautics
- Materials Research
- Reading Alloys
- Shieldalloy Corporation
- Titanium Alloy
- Var-Lac-Oid Chemical

In addition to the references listed in this report, the following parts from Gmelin's Handbook of Inorganic Chemistry (8th Edition) have been published so far and are pertinent:

System No. 57 (Nickel Part B)

Section 1 The Alloys of Nickel, 1965

Section 2 Compounds up to Nickel and Polonium, 1966

Section 3 Concluding Nickel Compounds, 1966.

These sections have German-English tables of content and English headings and sub-headings on the margins of the text.

Recent Research

Research in 1965 led to these developments in nickel:

- Improved nickel powder for making strip and other products
- A pilot-plant stage for continuously coating steel with nickel powder
- The first commercial application of a new high-strength age-hardening steel containing copper and 1 percent nickel

- Encouraging growth, with new applications ranging from die-casting dies to missile-booster cases, for the nickel maraging steels
- Opening of new markets for 9 percent nickel steel for cryogenic use as a result of advances in the use of liquefied nitrogen gas as a refrigerant
- Construction in Europe and North America of nuclear power plants utilizing reactor systems that make use of nickel stainless steels and nickel-chromium alloys.

Toxicity Information

Depending on the organism and the type of nickel compound, nickel can be beneficial or toxic. It is essential to some organisms. Injected nickel appears to be very toxic; however, it is not readily absorbed except in the case of nickel carbonyl. Nickel and its salts are considered by many as nontoxic, producing only a contact dermatitis in the sensitized individual. Nickel carbonyl has accounted for most of the acute toxicity of nickel. Recent studies have emphasized the carcinogenic properties of nickel and the possibility that hypersensitivities in the general environment is a growing concern.

In comparison to mercury, reviews and recent interest in nickel toxicology have been rather limited. Except where otherwise indicated, the following material is abstracted from the review of Browning(C-35), Stokinger(C-46) and Mastromatteo(C-43).

Incidence of Nickel Poisoning

Gefafer(C-39) gives the following list of potential occupational exposures for nickel and nickel salts:

Battery makers, storage
Cemented carbide makers
Ceramic makers
Disinfectant makers
Dyers
Electroplaters
Enamelers
Gas-mask makers
Ink makers
Jewelers
Magnet makers
Mond-process workers
Nickel-alloy makers
Nickel miners
Nickel refiners
Nickel smelters
Nickel workers
Oil hydrogenators
Organic-chemical synthesizers
Paint makers
Pen-point makers
Petroleum refinery workers
Spark-plug makers
Steel makers, stainless
Textile dyers
Vacuum-tube makers
Varnish makers

According to Browning(C-35), systemic poisoning from nickel salts is almost unknown, either from therapeutic or industrial usage. Nickel dermatitis has been reported in industrial workers, especially nickel platers, and its incidence appears to be rising. Fisher and Shapiro(C-40) reported that nickel is a very common cause of allergic contact eczematous dermatitis and may occur on almost any skin area. Most of these cases were not the result of industrial exposure but of wearing nickel-containing objects. Nickel-containing coins apparently rarely caused nickel dermatitis.

The chief industrial hazard of nickel is exposure to nickel carbonyl. Its acute potentialities were discovered soon after it first appeared in 1890. The occupational cancer occurring in men exposed to nickel powder "formed by decomposition of a gaseous nickel compound" has been a "prescribed" (compensable) disease in Great Britain since 1949. For the period 1923 to 1948, 47 cases of nasal cancer and 72 lung cancer were reported from the Welsh nickel refineries. Data in 1956 indicated that the risk of nickel workers dying from lung cancer was approximately 5 times the normal and that of sinus cancer approximately 150 times the normal.

Mastromatteo(C-43) recently reviewed the occupation aspects of nickel poisoning. He summarized the incidence of cancer in the Ontario Nickel Refinery for the period of 1930 to 1965. His data are presented in Table C-9. The 16 sinus-cancer deaths and the 37 pulmonary-cancer deaths are considerably higher than expected from population norms.

TABLE C-9. MORTALITY IN ONTARIO NICKEL-REFINERY WORKERS ACCORDING TO EXPOSURE GROUPS 1930-1965(C-43)

Exposure Group	Sinus-Cancer Deaths		Pulmonary-Cancer Deaths	
	Observed	Expected	Observed	Expected
Furnace workers	5	0.023	8	1.88
Other dust	--	0.029	4	1.89
Electrolytic workers	--	0.014	1	1.26
Nondust	--	0.011	--	1.07
Office	--	0.006	2	0.41
Mixed $<$ 3 yr in 1 and 2 + other work	2	0.035	6	2.57
Mixed $\geq$ 3 yr in 1 + other work	8	0.026	15	2.15
Mixed $\geq$ 3 yr in 2 + other work	1	0.022	1	1.47
Total	16	0.166	37	12.711

Pharmacology

Mechanism of Action. Many observers, according to Browning(C-35), support the idea that the toxicity of nickel is due to its capacity for inhibiting enzyme systems such as acid phosphates (Ohlmeyer, 1947) or to its interference with other enzyme systems. Apparently a comprehensive study of the enzyme reactions has not been undertaken. The skin-sensitization mechanism has been debated. Some observers consider the reaction to be an expression of epidermal sensitivity, others of an affinity of the stratum corneum for the metal. According to Browning(C-35), Wells stated in 1956 that the carboxyl groups of keratin in the stratum corneum play some part in retaining the nickel, while Nexmand believes that the vascular tissue of the coreum is also involved. The corrosive action of sweat on nickel may explain the ease of sensitization.

Sunderman and Hackett(C-48) recently reported inhibition of benzpyrene hydroxylase. Benzpyrene is a carcinogen found in tobacco smoke along with nickel. Therefore, there is the possibility that this might be one of the carcinogenic mechanisms in lung and sinus cancer.

Absorption, Distribution and Excretion(C-35). Absorption of nickel is slow and somewhat difficult from the gastrointestinal tract. No absorption into the body seems to take place from the skin in animals or humans; however, the skin of nickel-sensitive humans reacts with a nickel dermatitis. Orally administered nickel is excreted mainly in the feces (90 percent) and less so in the urine (10 percent). Injected nickel is excreted mainly in the urine.

The chief storage depots of administered nickel are in the spinal cord, brain, lungs and heart. Ware and his coworkers in 1954, using radioactive techniques, found that nickel is widely distributed in the organism and rapidly eliminated by both urine and feces, that of the urine being maximal in the first 4 hours.

Toxicology

Acute Poisoning. The chief industrial hazard of nickel is exposure to nickel carbonyl. The acute poisoning apparently has two phases: an initial attack of headache, dizziness, nausea, and vomiting, with a delayed syndrome ushered by retrosternal pain, tightness in the chest and dry cough, shortness of breath, rapid respiration, cyanosis, and extreme weakness. In cases described by Sundermann and Kincaid, the weakness was so great that respiration could only be sustained by oxygen therapy. In fatal cases, death occurred between 4 and 11 days, usually preceded by convulsions, sometimes by mental confusion.

The lesions resulting from lethal exposure have been mainly in the lung and brain. In the lungs, areas of hemorrhage, atalectasis, and necrosis were frequently found. There was also deposition of a brownish-black, non-iron-staining pigment in the histiocytes. In the brain, extensive damage in the form of dilated vessels, hemorrhages in the brain tissue, and meniges has been found.

The diagnosis of acute poisoning is made by the history of exposure accompanied by the characteristic signs and symptoms. Elevated blood and urine values should confirm the diagnosis. Imbus et al.(C-40) reported ranges for blood and urinary nickel, the median levels of which were 3.0 μg/100 ml and 7.4 μg/l, respectively.

The concentration of nickel in the urine remains high for at least 24 hours after severe exposure to nickel carbonyl and can possibly be correlated with the severity of exposure. In one study of 13 cases, 12 had values above normal, averaging 17 μg/100 ml, with a maximum of 41. In samples obtained post-mortem from two fatal cases, values were 52 and 400 micrograms.

Treatment with calcium disodium ethylenediamine tetraacetic acid has been tried without success in nickel carbonyl poisoning. BAL, 2, 3-dimercaptopropanol, provides only partial success. The therapeutic choice according to Sunderman is sodium diethyldithiocarbamate trihydrate.

Nickel Sensitization. The characteristic lesions begin by itching, which sometimes lasts for a week before the eruption appears. The primary eruption occurs on the part of the skin in which nickel has come in contact – earrings, suspenders, eyelets of shoes, etc. Stoddart(C-45) reported sensitization of patients from nickel-containing infusion cannulae, in which one patient had an anaphylatic reaction. Once acquired, the sensitivity appears to be permanent. Patch testing is used to detect sensitivity.

The problem of contact sensitivity to nickel is punctuated by a debate as to whether nickel and cobalt are cross-reacting or independent allergens (Pirila and Kajanne(C-44) and Epstein(C-37)). In Finland, both cobalt and nickel were found in cement in trace amounts (2 to 30 ppm); 415 workers with cement eczema were tested.

According to one report by Marcussen(C-41), the incidence of nickel dermatoses has shifted from the plating industry to other occupations, and particularly to non-occupational causes. A Danish survey of 621 cases showed that 4 percent were due to nickel plating, 9. 5 percent to other occupations, and 86. 5 percent were not due to occupation. The author emphasized the importance of preventive measures for the community more than for the adequately controlled industry.

Carcinogenic Effect. Mastromatteo(C-43) reviews the carcinogenic effect in some detail. Lung cancers have been described most frequently as squamous, the predominant variety in all industrially induced cancers. One case of the anaplastic type and one of the alveolar type were described among four cases by Williams in 1958. Nasal cancer, like that of the lung, is much less frequent now than in the early days of nickel refining employing nickel carbonyl (Mond process).

Environmental Hazards

Average and maximum concentrations of nickel monitored in the National Air Sampling Network of the Public Health Service during 1964 and 1965 were, respectively, 0. 034 and 0. 50 $\mu g/m^3$. Monitorings were carried out biweekly at 103 urban stations scattered throughout the United States. Concentrations of nickel monitored in the National Water Quality Network of the Public Health Service during 1960 and 1961 ranged from 0. 001 to 0. 07 mg/liter. Monitorings were carried out at approximately 120 stations representing 58 United States rivers.

Studies from the Jefferson Medical College Laboratory(C-47) have demonstrated the presence of nickel in tobacco smoke. These studies have established that pulmonary cancer may be induced in rats exposed to a single heavy concentration of nickel carbonyl as well as in rats exposed to repeated inhalations of sublethal concentrations for a period of a year. It is noteworthy that cancers were not observed in the experimental animals until 2 or more years after the initial exposure, and averaged 24 to 27 months after initial exposure in their recent report.

Computations indicate that the amount of nickel inhaled annually by a heavy smoker is several times the amount that is carcinogenic for the rat, an animal known to be unusually resistant to the development of pulmonary cancer.

The United States Public Health Service's drinking-water standards, according to McKee and Wolf(C-42), does not place any limit on nickel but Kirkor in Russia reported that the maximum permissible concentration is 1.0 mg/l. Metallic nickel or nickel salts are considered nontoxic relative to water-quality standards(C-42). Nickel may have secondary contamination effects in economic uses, as indicated by its tendency under acidic conditions to cause pitting in aluminum ware in combination with copper, cobalt, and chloride. Also, some nickel salts are toxic in low concentrations to microorganisms and fish.

Because of the large amount of nickel consumed annually, and because of the problems of hypersensitivity and cancer, it is imperative that an adequate evaluation of the ecology of nickel be made to establish where all of this nickel is going and whether it is a health hazard.

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Agriculture
Aircraft
Automotive
Chain
Corrosion
Diesel
Electrical and electronics
Gears
Glass
Machine tools
Marine
Mining
Paper and pulp
Petroleum
Power
Railway
Space
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APPENDIX D

FLUOROCARBONS

APPENDIX D

FLUOROCARBONS

Economics Information

Production(D-1 – D-6)*

Fluorochemical Plants. The nation's fluorocarbon industry is moving at a fast pace. Plant capacity in 1966 exceeded 600 million pounds. The major producers and plant capacities are given in Table D-1. Classes of fluorocarbons produced are shown in Table D-2.

TABLE D-1. BASIC PRODUCERS OF FLUOROCARBONS IN THE UNITED STATES

Company	Trade Names of Principal Fluorochemicals	Plant Capacity, 10^6 lb/yr	Plant Locations
Allied Chemical Corporation	Genetron Genesolve Halon TFE Plaskon CTFE	120	Baton Rouge, Louisiana Elizabeth, New Jersey Danville, Illinois El Segundo, California
E. I. du Pont de Nemours and Company	Freon Teflon TFE Viton	350	Antioch, California Carney's Point, New Jersey East Chicago, Indiana Louisville, Kentucky Parkersburg, West Virginia
Kaiser Aluminum and Chemical Corporation	Kaiser	25	Gramercy, Louisiana
Minnesota Mining and Manufacturing Company	Kel-F#81 and 82 Fluorei	5	Decatur, Alabama
National Rolling Mills Company	--	25	Malvern, Pennsylvania
Pennsalt Chemicals Corporation	Istron Kynar	60	Calvert City, Kentucky King of Prussia, Pennsylvania
Thiokol Chemical Corporation	Thiokol TFE	2	Moss Point, Mississippi
Union Carbide Corporation	UCON	50	Institute, West Virginia

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* References for Appendix D will be found on p D-14.

TABLE D-2. CLASSIFICATION OF FLUOROCARBONS

Company	Trade Name	Number(a)
Allied Chemical Corporation	Genetron	11, 12, 13, 14, 21, 22, 23, 112, 113, 114, 115, 142b, 152a, 218, 1112a, 1113, 1132a, 12/11, 12/114, 142b/114
E. I. du Pont de Nemours & Company	Freon	11, 12, 13, 13B1, 14, 21, 22, 23, 112, 112a, 113, 114, 114B2, 115, 116, 214, 215, 216, C318, 502, 503, E1, E2, E3, E4, E5, C51-12, 116/318, 116/318, 12B2, 216B2
Kaiser Aluminum and Chemical Corporation	Kaiser	11, 12, 22
National Rolling Mills Company	--	11, 12
Pennsalt Chemicals Corporation	Isotron	11, 12, 13, 22, 113, 114
Union Carbide Corporation	UCON	11, 12, 22, 113, 114

(a) In this system, the digit on the right gives the number of fluorine atoms in the molecule. The second digit from the right is one more than the number of hydrogen atoms. The third digit from the right is one less than the number of carbon atoms. When this number is 0, as in one-carbon compounds, it is omitted. All other available positions in the molecule are filled with chlorine. For example, dichlorodifluoromethane is number 12; dichlorotetrafluoroethane is number 114; etc. Cyclic compounds are indicated by the letter C preceding the number. When bromine is present, the same numbering system is used, followed by the letter B and a number indicating the number of chlorine atoms replaced by bromine. For example, bromotrifluoromethane is numbered 13B1. Unsaturated products are indicated by the number 1 in the fourth place from the right – for example, chlorotrifluoroethylene would be 1113.

Construction projects (capacity not reported) also reflect growth of the fluorocarbon industry. Some of these are:

- Racon, Incorporation, Houston, Texas, has licensed a Japanese process for the manufacture of Fluorocarbons 11, 12, and 22. Raw materials are chloroform, carbon tetrachloride, and hydrofluoric acid.
- Minnesota Mining and Manufacturing Company (3M) recently built a 4.5 million dollar fluorocarbon plant at Decatur, Alabama. Much of its output will consist of Scotchguard products; the remainder, fluorocarbons.

Methods of Preparation. Fluorocarbons, or more correctly fluorohydrocarbons, can be produced by direct fluorination using a high-valence-metal fluoride such as cobalt trifluoride: $-CH_2- + 4\,CoF_3 \rightarrow -CF_2- + 4\,CoF_2 + 2\,HF$. The method has been used to prepare fluorohydrocarbons containing from one to more than twenty carbon atoms. Fluorohydrocarbons have also been made commercially by the electrolysis of solutions of alcohols, acids, or amines in anhydrous hydrogen fluoride. For example, electrolysis of a solution of acetic acid in anhydrous hydrogen fluoride using a nickel anode gives fluoroform and carbon tetrafluoride.

The simpler fluorohydrocarbons can be prepared by the reaction of anhydrous hydrogen fluoride with a chlorofluorocarbon at elevated temperatures using an appropriate catalyst such as antimony fluoride.

$$CCl_2F_2 + 2\ HF \rightarrow CF_4 + 2\ HCl$$

$$CHCl_3 + 3\ HF \rightarrow CHF_3 + 3\ HCl$$

$$3\ CHF_3 \xrightarrow{\Delta} C_3F_6 + 3\ HF\ .$$

Fluorinated ethylenes are manufactured commercially by the pyrolysis of a saturated compound. For example, tetrafluoroethylene $CF_2{=}CF_2$ is obtained by heating $CHClF_2$ or CHF_3:

$$CHClF_2 \xrightarrow{\Delta} CF_2{=}CF_2 + 2\ HCl$$

$$2\ CHF_3 \xrightarrow{\Delta} CF_2{=}CF_2 + 2\ HF\ .$$

Teflon has also been obtained by pyrolysis of a mixture of CHF_2Cl and $CHFCl_2$; CHF_3, CF_2ClCF_2Cl in presence of a catalyst, and electrolysis of low-molecular-weight perfluorinated hydrocarbons.

Among newer developments of simple polymers is the preparation of polyvinyl fluoride $(CHFCH_2)_n$ and polyvinylidene fluoride $(CF_2CH_2)_n$ (Pennsalt's Kynar). The monomers are probably prepared as follows:

$$HC{\equiv}CH + HF/\text{catalyst} \rightarrow CHF{=}CH_2$$

$$HC{\equiv}CH + 2\ HF/\text{catalyst} \rightarrow CH_3CHF_2$$

$$CH_3CHF_2 + Cl_2 \rightarrow CH_3CClF_2 + HCl$$

$$CH_3CClF_2 \xrightarrow{\Delta} CH_2{=}CF_2 + HCl\ .$$

Chlorofluorohydrocarbons are manufactured by the successive replacement of chlorine by fluorine using hydrogen fluoride. Partially fluorinated antimony pentachloride is the catalyst. For example, chlorotrifluoroethylene, the monomer for 3 M's Kel-F is prepared as follows:

$$CCl_3CCl_3 + HF/Sb^{+5} \rightarrow CClF_2CCl_2F$$

$$CClF_2CCl_2F + Zn/EtOH \rightarrow CClF{=}CF_2\ .$$

Bromofluoro hydrocarbons can be obtained by reactions of which the following are typical:

$CHF_3 + Br_2 \rightarrow CBrF_3 + HBr$

$CHClF_2 + HBr \rightarrow CHBrF_2 + CBrClF_3$

$CBr_4 + 2\ HF \rightarrow CBr_2F_2 + 2\ HBr.$

Bromine can be added to $CF_2 = CF_2$ to form $CBrF_2-CBrF_2$.

Manufacturers and Distributors. Fluorocarbon manufacturers/distributors include:

Aldrich
Allied Chemicals Corporation, General Chemical Division
Allied Chemicals Corporation, Plastics Division
American Hoechst
E. I. du Pont de Nemours & Company, Incorporated, "Freon" Products Division
E. I. du Pont de Nemours & Company, Incorporated, Petroleum Chemicals Division
Halocarbon Products Corporation
Hynes Chemical Research
Westinghouse Electric Corporation, Industrial Electronics Division
International Selling
K & K Laboratories, Incorporated
Kaiser Chemicals
Matheson Company, Incorporated
McGee Chemicals Company
Peninsular Chem. Research, Incorporated
Pennsalt Chemicals Corporation
Pierce Chemical Corporation
Minnesota Mining and Manufacturing Company
National Rolling Mills Company
Thiokol Chemical Corporation
Union Carbide Corporation, Olefins Division
Wateree Chemical

Fluoroplastics manufacturers/distributors include:

Fluoroplastics-CTFE Fluorocarbon

Allied Chemical Corporation (New York, N. Y.)
Allied Chemical Corporation, Plastics Division
Applied Plastics Company, Incorporated
Axel Plastics Research Laboratories, Incorporated
Chemical Coatings and Engineering Company, Incorporated
Contours Unlimited, Incorporated
Liquid Nitrogen Processing Corporation
Minnesota Mining and Manufacturing Company
Raybestos Manhattan, Incorporated
Whitford Chemical Corporation

Fluoroplastics-FEP Fluorocarbon

Axel Plastics Research Laboratories, Incorporated
Contours Unlimited, Incorporated
E. I. du Pont de Nemours and Company, Incorporated
Liquid Nitrogen Processing Corporation
Lorben Corporation
Polymer Corporation, The Export-Polypenco Division
Raybestos Manhattan, Incorporated
Whitford Chemical Corporation

Fluoroplastics-Fluorohalocarbons

Allied Chemical Corporation
Axel Plastics Research Laboratories, Incorporated
Contours Unlimited, Incorporated
Liquid Nitrogen Processing Corporation
Raybestos Manhattan, Incorporated

Fluoroplastics-Polyvinyl Fluoride

Axel Plastics Research Laboratories, Incorporated
Contours Unlimited, Incorporated
E. I. du Pont de Nemours and Company, Incorporated
Watson-Standard Company

Fluoroplastics-Polyvinylidene Fluoride

Contours Unlimited, Incorporated
E. I. du Pont de Nemours and Company, Incorporated
Ferro Corporation, Cordo Division
Pennsalt Chemicals Corporation

Fluoroplastics-TFE Fluorocarbon

Allied Chemical Corporation
Allied Chemical Corporation, Plastics Division
Axel Plastics Research Laboratories, Incorporated
Chemical and Power Products, Incorporated
Contours Unlimited, Incorporated
Davies Nitrate Company, Incorporated
E. I. du Pont de Nemours and Company
Liquid Nitrogen Processing Corporation
Metachem Resins Corporation, Mereco Products Corporation Division
Miller-Stephenson Chemical Company, Incorporated
Pennsalt Chemicals Corporation
Raybestos Manhattan, Incorporated
Thiokol Chemical Corporation, Chemical Division
Watson-Standard Company
Whitford Chemical Corporation

Use Pattern(D-7 -- D-12)

Nonplastics. In today's fluorohydrocarbon, industry the following five compounds are among the best sellers:

Fluorocarbon-12 (Dichlorodifluoromethane; CCl_2CF_2). CCl_2CF_2, which boils at 216 F, accounts for over half of the United States' fluorocarbon production. It was the first of the fluorocarbon aerosol propellants and is now used either alone or together with such fluorocarbons as 11 and 114. It is widely used in household and commercial refrigeration and air conditioning.

Fluorocarbon-11 (Trichloromonofluoromethane; CCl_3F). CCl_3F, which boils at 74.8 F, rose to prominence when low-pressure "beer-can" aerosol containers were introduced. It is widely employed in commercial air conditioning, as a blowing agent for plastic foams, and in cooling industrial-process water and brine.

Fluorocarbon-22 (Chlorodifluoromethane; $CHClF_2$, which boils at -41.4 F, is used in air-conditioners, home freezers, and industrial refrigeration. Fluorocarbon-22 is also used in making tetrafluoroethylene, the monomer for Teflon plastic.

Fluorocarbon-113 (Trichlorotrifluoroethane). This compound boils at 117.6 F and is used as a refrigerant in commercial and industrial air-conditioning. It is partially dechlorinated to make the monomer for Kel-F.

Fluorocarbon-114 (Dichlorotetrafluoroethane). This compound boils at 38.4 F and is especially useful where an aerosol product contains a large amount of water, as in shaving creams and colognes, and where corrosion of the container might be a problem. It is also used industrially in air-conditioning and process cooling.

Fluorocarbon usage in 1963 and 1966, and projected usage in 1970, is shown for various categories in Table D-3. Mainly because of high cost, there probably will be a

TABLE D-3. FLUOROCARBON CONSUMPTION

Millions of Pounds

Outlet	1963	1966 (Estimated)	1970 (Estimated)
Aerosols	200	300	280
Refrigerants	120	150	190
Foam-blowing agents	20	50	90
Resins	40	65	90
Solvents, dielectric fluids, and degreasing fluids	10	15	15
Exports and other uses	20	20	20
Total	410	600	685

decline in the use of fluorocarbons by the aerosol industry. During 1965, 1.8 billion aerosol units[*] were manufactured, of which 1.7 billion units were in the nonfood category. A sizable portion of these used fluorocarbons in such categories as personal hygiene and cosmetic products, household products, industrials, animal products, insect sprays, automotive specialties, and spray coatings.

Most successful of the food aerosols is whipped cream. Food toppings and flavors have also been marketed and some dozen or more products are under careful study and test. Only fluorocarbon propellants C-318 and 115 have been cleared for food use by FDA. C-318 has such a low vapor pressure that it expels food products satisfactorily only at room temperature. Fluorocarbon 115 has a high enough vapor pressure to expel refrigerated food products. Generally, foods thus far marketed have been propelled by compressed soluble gases – carbon dioxide, nitrous oxide, and nitrogen. A number of food-aerosol products now being test marketed conceivably might employ fluorocarbon propellants. They include:

- Barbecue sauce
- Cake frosting
- Canape spread[**]
- Catsup
- Cheese spread
- Decorative icing
- Extracts
- Fruit puree (whipped)
- Honey (whipped)
- Juice concentrate
- Whipped cream topping[**]
- Mayonnaise
- Meat tenderizer
- Meringue
- Milk flavoring[**]
- Mustard
- Pancake batter
- Popcorn seasoning
- Salad dressing (liquid spray)
- Sour cream
- Syrup (flavored)

The refrigeration market for fluorocarbons is expected to grow, aided by the increasing use of room and central air-conditioning units. Blowing agents should provide a sizable and growing outlet for fluorocarbons at least through 1970. Resins will continue to provide a growing outlet for fluorocarbons. During 1966, production of fluorocarbon resins was about 25 million pounds, representing an outlet for nearly 65 million pounds of fluorocarbons. By 1970, consumption of fluorocarbons in resins may total 90 million pounds. Solvent and degreasing applications for fluorocarbons are expected to show moderate growth. Exports for fluorocarbons are not likely to grow.

A potentially large use for fluorocarbons that has not been categorized is the coin-operated dry-cleaning-solvent market. In 1962 it was predicted that trichlorotrifluoroethane (Freon 113) would challenge perchloroethylene in this field. If this truly takes hold it could serve as a multimillion-pound outlet for fluorocarbons.

Three fluorochemicals continue to be used as general anesthetics. They are Fluroxene (Fluoromar) 2,2,2-trifluoroethyl vinyl ether, Halothane (Fluothane) 2-bromo-2-chloro-1,1,1-trifluoroethane, and Methoxyflurane (Penthrane) 2,2-dichloro-1,1-difluoroethyl methyl ether. Because these anesthetics are halogenated compounds, it has been recognized that acute or delayed liver damage might occur after their administration. However, a direct relationship between the administration of these drugs and the subsequent development of liver damage has not been demonstrated.

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[*] The estimate for 1966 is 2.2 billion units.

[**] Now on the market.

Plastics.(D-13-D-19) Fluorocarbon polymers, or fluoroplastics, are paraffinic hydrocarbon polymers in which all or part of the hydrogen atoms have been replaced by fluorine or another halogen.

In the order of decreasing fluorine substitution and increasing processability, these materials include polytetrafluoroethylene (PTFE), fluorinated ethylenepropylene (FEP), the chlorotrifluoroethylenes (CTFE), and polyvinylidene fluorides. Also available are several copolymers of halogenated and fluorinated hydrocarbons, including fluorinated elastomers.

Approximately 20 million pounds of polytetrafluoroethylene (TFE) were used in 1966. Major applications were in the following categories:

- Wire and cable insulation for connectors, coaxial spacers and other components, stand-off and feed-through insulators, and motor-slot insulation
- Gaskets, seals, valves, diaphragms, chemical hose, bellows, and expansion joints
- Laboratory ware such as beakers, watch glasses, and stopcocks
- Sealant for threaded pipe joints
- Packings, bearings, and piston rings
- Tape and sheeting for conveyor chutes and similar applications to reduce friction
- Coatings to provide a nonstick surface on rolls, pans, and domestic cookware.

Four industries take most of the polytetrafluoroethylene resins, as categorized in Table D-4.

TABLE D-4. INDUSTRIAL USE OF TFE POLYMERS

Millions of Pounds

Industry	1963	1966 (Estimated)	1970 (Projected)
Granular Grades			
Aerospace	1.25	2.00	2.50
Chemical process	2.75	3.75	5.00
Electrical and electronic	2.00	3.25	5.00
Mechanical goods	1.00	2.25	4.00
Paste and Dispersion Grades			
Aerospace	1.00	1.50	2.00
Chemical process	1.00	1.75	2.75
Electrical and electronic	3.25	4.75	8.00
Miscellaneous	0.25	0.40	0.75
Total	12.50	20.25	30.00

An additional 5 million pounds of fluorohydrocarbon consumption is accounted for by Du Pont's Teflon FEP (a copolymer of tetrafluoroethylene and hexafluoropropylene, Du Pont's Viton (a copolymer of vinylidene fluoride and hexafluoropropylene), Allied's Plaskon, and 3M's Kel-F (polymers of chlorotrifluoroethylene) and Pennsalt's Kynar (a polymer of vinylidene fluoride). Teflon FEP accounted for about 3.0 million pounds. Output of the others totaled 2.0 million pounds. Applications for these four materials are as follows:

Viton

- General molded goods
- Hose
- Fabric coating
- Sealants and caulks

Fluorinated Ethylene Propylene FEP (Teflon FEP)

- Insulation on wire and cable
- Corrosion-resistant linings in pipe and fittings, laboratory ware and bottles
- Films and sheeting in corrosion-resistant linings for chemical tanks and equipment
- Antistick coatings laminated to metal or other substrates
- Heat-shrinkable coatings

Chlorotrifluoroethylene (CTFE) (KEL-F81, KEL-F82 and Plaskon CTFE)

- Electrical and electronic components
- Corrosion-resistant linings in valves and pumps
- Insulation on wire and cable
- Tubings and films for the packaging of drugs and pharmaceutical items
- Coating systems for corrosion protection on chemical-process equipment
- Seals and gaskets for cryogenic equipment, where service at -423 F is required.

Polyvinylidene Fluoride (Kynar)

- Wire and cable insulation
- Electronic and electrical components
- Irradiated shrinkable tubing
- Chemical-process equipment components
- Aerospace components in contact with storable propellants
- Long-life durable finish for exterior siding.

Recent Research in Fluorochemicals

- Two polyvinylidene fluoride-based coatings – Du Pont's Du Lite and De Soto Chemical Coatings' Fluropon – were developed to protect metal sidings on nonresidential buildings.

- Dalvor, a polyvinyl fluoride coating resin developed by Diamond Alkali recently found its first commercial outlet as a drum lining.
- Improved nonstick fluoropolymer coatings called DR were developed by Du Pont.
- Fluorochemical paper sizes were developed for possible use in greaseproof barriers in contact with human or pet foods.
- Bronze-filled fluorocarbons were evaluated as lubricants at liquid-hydrogen temperature.
- A fuel cell using conducting porous Teflon fluorocarbon electrodes has been developed for the Army by General Electric.
- Researchers at the National Bureau of Standards reported the synthesis of new fluoropolymers.
- A Teflon spray was developed for sealing and lubricating pipe threads. It can be used on any piping metal including aluminum, galvanized steel, and stainless steel.
- A new series of fluorocarbons are now available from Hynes Chemical Research.
- A technique was developed for spray-coating metal surfaces with Teflon and other fluorocarbon plastics.
- A family of five stable, inert fluorocarbon liquids, E 1 through E 5, has been developed by Du Pont as dielectric coolants, insulating media in electrical and electronic equipment, plasticizers, sealants, and hydraulic fluids.
- 3, 3, 3-Trifluoropropylene and perfluoropropylene epoxide, both gases, are now available from Calgon Corporation.

Toxicity Information

Zapp's review(15) of the "Toxic and Health Effects of Plastics and Resins", and Clayton's chapter on the Mammalian Toxicology of Organic Compounds Containing Fluorine" – Handbook of Experimental Pharmacology, present in principle many of the important aspects of toxicity of fluorocarbons. Table D-5 presents a summary of the toxicity of the fluorocarbons studied in this report. The toxicities of several fluorinated alkenes are given in Table D-6. Perfluoroisobutylene, a toxic pyrolysis product of Teflon, is included also.

TABLE D-5. TOXICITIES OF COMMERCIALLY IMPORTANT FLUOROCARBONS

Compound	Use	Levels	Toxicity[(a)]
Chlorodifluoromethane	Refrigerant	--	U, DH
Chlorotrifluoroethylene	Monomer	--	U, DH
Chlorotrifluoroethylenes (CTFE, polychlorotrifluoroethylene)	Plastic	--	N, DH, esp. over 300 C
Dichlorodifluoromethane	Aerosol, refrigerant	TLV (max) = 1,000 ppm	O-S, DH
Dichlorotetrafluoroethane	Aerosol	TLV (max) = 1,000 ppm	Slight to moderate DH
"Fluorides"	Reactants and decomposition products	TLV = 2.5 mg/m^3	H
Fluorinated ethylenepropylene (FEP, Teflon)	Plastic	--	DH
Fluorine	Reactant and pyrolysis product	TLV = 0.1 ppm	High
Fluoroxene	Anesthetic	--	S
Freon 115-chloropentafluoroethane	Aerosol		
Halothane	Anesthetic	--	S
Hexafluoropropylene	Monomer	LC_{50} = 3,000 ppm	O, DH
Methoxyflurane	Anesthetic	--	S
Perfluoroisobutylene	Teflon pyrolysis product	LC_{50} = 0.5 ppm	High
Polyvinylidene fluoride	Plastic	--	DH
Polytetrafluoroethylene (PTFE, Teflon)	Plastic	Nonvolatile, decomposes with heat	N, DH above 750 F
Tetrafluorethylene	Monomer	LC_{50} = 40,000 ppm	Low DH
Trichloromonofluoromethane	Refrigerant	TLV (max)	S, DH
Vinyl fluoride	Monomer	LC_{50} = 800,000 ppm	Low
Vinylidene fluoride	Monomer	LC_{50} = 128,000 ppm	Low

(a) Toxicity ratings used by Sax (1963): 0 = none; S = slight; M = moderate; U = unknown (normal conditions), DH = danger hazard (toxic pyrolysis products); TLV = threshold-limit values American Conference of Governmental Industrial Hygienists).

TABLE D-6. TOXICITY OF SEVERAL FLUORINATED ALKENES

Compound	LC_{50}, ppm by vol
Vinyl fluoride $CH_2{=}CHF$	800,000
Vinylidene fluoride $CH_2{=}CF_2$	128,000
Tetrafluoroethylene $CF_2{=}CF_2$	40,000
Hexafluoropropylene $CF_3CF{=}CF_2$	3,000
Perfluoroisobutylene $(CF_3)_2C{=}CF_2$	0.5

Monomeric Aerosols, Refrigerants, and Anesthetics

Most of these compounds under ambient conditions are relatively nontoxic. As a generalization, the more fluorine atoms in a saturated compound, the less toxic it is. Conversely, toxicity increases in an unsaturated compound with increase in fluorine, chlorine, or bromine. The relationship to toxicity is probably dependent on molecular activity conferred by the double bond and is independent of the degree of fluorination per se. This is illustrated in Table D-6, which shows the lethal concentrations of several fluorinated alkenes.

Gefafer(D-25) summarizes briefly some of the symptomatology of fluorocarbon exposure. Fluorocarbons may produce very mild irritation of the upper respiratory tract. If chlorine-containing fluoromethanes come into contact with open flame or hot metal, the decomposition products hydrogen chloride, hydrogen fluoride, phosgene, sulfur dioxide, and chlorine may cause severe irritation. The toxicity of many of these decomposition products is substantially documented in the literature. Systemically, certain of the fluorocarbons may produce mild central-system depression, possibly due in part to displacement of air, with resultant hypoxia. The route of entry into the body is by inhalation. Although there are several reports of industrial poisoning, these are relatively few. These are discussed in brief by Clayton.(D-22)

The literature on the use and the effects of fluorocarbon anesthetics such as Halothane, Fluoroxene, and Methoxyflurane is extensive and has been recently summarized in Goodman and Gilman.(D-26) Halothane, perhaps the most popular anesthetic today, has been found to be quite safe when properly administered. The possible influence of a fluoroalkene contaminants in causing sharp increases in acute toxicity has been substantiated in detailed studies on rats and dogs.(D-30) Impurities arising during the manufacture of Halothane have been identified.(D-22)

Plastic Fluorocarbons

The fluorocarbon plastics present a relatively unique and complex set of problems. Under ordinary conditions the pure polymer is nontoxic. However, the residual, unreacted monomers, added plasticizers, stabilizers, etc., can provide potential toxicities. This is important in the consideration by the Food and Drug Administration of approvals for the use of plastics as food containers. Tomatis and Shubili(D-35) reported on the carcenogenicity of subcutaneous Teflon implants.

Important and illustrative is the case of Teflon (polytetrafluoroethylene). Inhalation of heated freshly generated Teflon dust can produce a polymer fever, which is characterized by chills, fever, and aches in the muscles and joints. The condition is usually over within 24 hours after removal from the exposure atmosphere. Polymer fever "mimics and is confused as influenza".(D-27, D-34)

Other, more dangerous conditions are possible during the conflagration of Teflon and other synthetic polymers. Teflon will not burn spontaneously but will decompose if sufficient heat is applied externally. Teflon TFE resins are among the most thermostable of all the synthetic plastics and resins, being rated for continuous use at 260 C. The TFE resin softens at 327 C, but can stand brief exposures to temperatures high as 540 C. It does not liquefy on exposure to heat, but gives off gases and particulate matter referred to as sublimate. As the temperature is increased, various toxic products are given off, including large quantities of the monomer, tetrafluoroethylene, other fluorocarbon gases of 3-, 4-, and 5-C atoms, HF, perfluoroisobutylene, and, depending on the amount of oxygen available, CO_2 and CO. Table D-7 contains toxicity data on perfluoroisobutylene.

TABLE D-7. SUMMARY OF SINGLE EXPOSURES OF RATS TO PERFLUOROISOBUTYLENE

Nominal Concentration, ppm by volume	Length of Exposure hr:min	Mortality Ratio, No. dead/ No. exposed	Clinical Signs	Pathological Changes
1.0	4:15 5:20	2/2	Dyspnea, cyanosis, gasping convulsions.	Acute pulmonary edema
0.5	6:00	2/2	Slight dyspnea after exposure. Both died overnight.	Acute pulmonary edema
0.3	6:00	0/2	None during exposure. Slight increase in respiration rate and weight loss next day. Recovered thereafter.	None observed 9 days after exposure

Source: Haskell Laboratory, unpublished data.

Polymer fume fever can be induced by fumes from Teflon at 300 C or more(D-27). Studies in which animals were used for experimentation have shown fumes from Teflon and other plastics to be highly toxic.(D-27, D-29) More recently, Robbins and Ware reported a case of pulmonary edema from Teflon fumes.(D-32)

Environmental Hazards

No review and evaluation of the actual or potential hazards arising from the industrial and commercial use of fluorocarbons was found in the literature. Probably none has been published, according to a personal communication from Dr. John A. Zapp, Jr., an authority on toxic effects of plastics. In the absence of such a review, the problem was analyzed by examining pertinent items collected in a literature search. Four groups of monomeric or polymeric fluorocarbons were examined with respect to possible hazards from their uses as aerosols, refrigerants, anesthetics, and plastics. Relatively adequate information was found on processing and utilization of these materials. Toxicity data, as well as industrial poisoning cases, are sparse. The "quick-reference texts" offer little toxicological information. What is available suffers from the lack of adequate clinical experience.

A huge amount of fluorocarbon compounds are used in today's economy, and the final products end up as waste materials, including waste from industrial processes, municipal waste-treatment products, and, possibly, volatiles in the atmosphere. A buildup of degradation products of fluorocarbons in water supplies would be detected as water-soluble fluorides in the monitoring of the National Water Quality Network of the Public Health Service. Although the National Air Sampling Network of the Publis Health Service does not report fluorine-containing organic compounds, such compounds would be expected to appear in the organic fraction. The volatility and possible escape of such products as aerosols and refrigerants indicates that they may be accumulating undetected in our environment. However, their low toxicity implies that extensive studies do not hold a high priority at this time. Because of the magnitude of the consumption of fluorocarbons, a preliminary study to establish base levels of fluorine-containing contaminants might well be in order. The waste products of other synthetic fluorinated chemicals might prove upon investigation to be a more important health hazard than the fluorocarbons.

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APPENDIX E

PULP AND PAPER CHEMICALS

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APPENDIX E

PULP AND PAPER CHEMICALS[(E-1 – E-12)*]

Economics Information

Location and Capacity of Pulp and Paper Mills

Pulp and paper mills are widely distributed throughout the United States. Table E-1 shows the number of pulp and paper mills in each state. The information on pulp mills is broken down to distinguish between ground wood mills, which use no chemicals, and chemical pulp mills. The chemical mills are subdivided according to the types of chemical processes used. Table E-2 supplements the information in Table E-1 by showing cumulative daily capacities of pulp and paper mills by states and by types of pulping processes in each state. Thus these tables indicate qualitatively the relative amounts and the use pattern of pulp and paper chemicals.

Domestic Production of Pulp and Paper Products

Statistical data on the United States production of pulp, paper, and paperboard also contributes peripheral information related to the use pattern for chemicals. Table E-3 shows production of wood pulp by grades for the years 1960-1965. Total pulp production has increased each year during the six-year period. Similarly Table E-4 gives the production of paper and board by grades for the same six years. Supplementing Tables E-3 and E-4, Table E-5 gives the geographical distribution of pulp, paper, and paperboard production for the year 1964 only.

Additional details on exact mill locations, their products, production equipment, and personnel can be found in Post's Pulp and Paper Directory (1966), and Lockheed's Directory of the Paper Industry (1966).

Use Pattern

Papermaking chemicals fall roughly into three distinct classes used with the operations of pulp processing, pulp bleaching, and paper and paperboard manufacture.

Pulp Processing. Of the three basic pulping processes (sulfite, neutral sulfite-semichemical, and kraft), the sulfite process is gradually losing its position as one of the major types of pulp processes. The lack of growth is attributed to the types of raw materials required (175 pounds of sulfur and approximately 150 pounds of lime per ton of pulp), to waste-liquor recovery difficulties, and to high material costs. The recent switch from lime to soluble bases, such as magnesium hydroxide or ammonium hydroxide, as a raw material for sulfite cooking liquor offers only a temporary solution. Present consumption of ammonia in the sulfite process is estimated at 65,000 tons.

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*References for Appendix E will be found on p E-20.

TABLE F-1. LOCATION AND TYPES OF PULP AND PAPER MILLS IN THE UNITED STATES

State	All Paper Mills	All Pulp Mills	Pulp Mills		Chemical Mills				
			Groundwood	Chemical	Sulfite	Sulfate	Soda	Semi-Chemical	Other
Alabama	11	12	3	9		8		1	
Alaska	--	2		2	2				
Arizona	2	2	1	1		1			
Arkansas	11	6	1	5		5			
California	32	5	1	4		3		1	
Colorado	1	--							
Connecticut	25	--							
Delaware	6	--							
District of Columbia	2	--							
Florida	13	9		9		8			1
Georgia	18	10		10		9		1	
Hawaii	1	--							
Idaho	2	1		1		1			
Illinois	27	1		1					1
Indiana	16	1		1				1	
Iowa	3	2		2				2	
Kansas	2	--							
Kentucky	1	--							
Louisiana	18	15	2	13		7		5	1
Maine	22	28	11	17	8	7	1	1	
Maryland	8	1		1		1			
Massachusetts	66	1		1			1		
Michigan	53	12	3	9	1	5		3	
Minnesota	11	8	4	4	2	1			1
Mississippi	8	5	1	4		3			1
Missouri	8	--							
Montana	1	1		1		1			
New Hampshire	28	2		2	1	1			
New Jersey	37	--							
New Mexico	1	--							
New York	89	18	9	9	4	2	2		1
North Carolina	11	4		4		3		1	
Ohio	46	2		2		1		1	
Oklahoma	5	--							
Oregon	22	15	3	12	6	5		1	
Pennsylvania	53	12	1	11	2	4	1	3	1
Puerto Rico	2	1		1					1
Rhode Island	2	--							
South Carolina	5	5	1	4		3		1	
Tennessee	12	8	1	7		1	2	2	2
Texas	13	6	3	3		3			
Vermont	10	2	2						
Virginia	16	10	1	9		4		4	1
Washington	23	30	7	23	12	7		1	3
West Virginia	3	--							
Wisconsin	42	39	15	24	14	3		5	2
Totals	795	276	70	206	52	97	7	34	16

TABLE E-2. DAILY CAPACITY OF PULP AND PAPER MILLS IN THE UNITED STATES[a, b]

In Tons

State	Paper and Board	Sulfite Pulp	Sulfate Pulp	Soda Pulp	Semichemical	Groundwood	Other Pulps
Alabama	6,460		4,570		180	1,090	
Alaska		1,150					
Arizona	285		265			175	
Arkansas	2,975		2,575			400	
California	5,088		900		240	40	
Colorado	100						
Connecticut	1,547						
Delaware	224						
District of Columbia	24						
Florida	6,875		8,150				375
Georgia	10,823		9,570		300		
Idaho	590		800				
Illinois	3,436						45
Indiana	1,255				130		
Iowa	500				360		
Kansas	190						
Kentucky	25						
Louisiana	8,607		5,885		1,010	393	75
Maine	6,118	1,698	2,205	150	320	2,775	
Maryland	1,777		700				
Massachusetts	3,620			56			
Michigan	8,104	170	985		860	213	
Minnesota	3,785	295	285			806	50
Mississippi	1,415		1,170			200	120
Missouri	490						
Montana	700		700				
New Hampshire	1,689	110	400				
New Jersey	4,371						
New Mexico	30						
New York	7,751	560	240	220		760	130
North Carolina	4,319		3,020		260		
Ohio	6,953		540		185		
Oklahoma	725						
Oregon	5,782	910	3,355		25	855	
Pennsylvania	6,370	100	775	75	610		25
Puerto Rico	180						100
Rhode Island	347						
South Carolina	3,995		3,935		480	150	
Tennessee	3,352		450	425	299	850	548
Texas	2,914		1,980			825	
Vermont	480					120	
Virginia	4,181		3,590		1,020	175	400
Washington	7,881	3,508	3,783		98	910	440
West Virginia	227						
Wisconsin	8,051	1,604	770	—	965	1,166	26
Totals	144,611	10,105	62,138	926	7,342	11,903	2,334

(a) Compiled from Post's Directory (1966).

(b) 52 paper mills and 6 pulp mills did not report capacity.

TABLE E-3. UNITED STATES PRODUCTION OF WOOD PULP BY GRADES, 1960 TO 1965[a]

Thousands of Short Tons

	1960	1961	1962	1963	1964	1965[b]
Total[c,d]	25,316	26,523	27,908	30,121	32,429	33,296
Special Alpha and Dissolving Grades	1,138	1,195	1,267	1,371	1,457	1,486
Bleached Sulfite	2,045	2,006	2,056	2,180	2,203	2,289
Unbleached Sulfite	533	567	509	510	483	500
Bleached Sulfate	5,032	5,405	5,863	5,728	6,438	7,249
Semibleached Sulfate	877	902	921	1,712	1,758	1,491
Unbleached Sulfate	8,681	9,115	9,517	10,502	11,810	11,774
Soda	420	436	425	390	350	229
Groundwood	3,292	3,208	3,397	3,468	3,596	3,920
Semichemical	1,991	2,352	2,543	2,629	2,712	2,885
Defibrated or Exploded	1,205	1,225	1,250	1,481	1,479	1,303

(a) Source: Bureau of the Census, Industry Division.

(b) Preliminary.

(c) Includes figures for Alaska.

(d) Addition of values may not give totals because figures have been rounded to the nearest thousand.

TABLE E-4. UNITED STATES PRODUCTION OF PAPER AND BOARD BY GRADES, 1960 TO 1965

Thousands of Short Tons

	1960	1961	1962	1963	1964	1965$^{(a)}$
All Grades, Total	34,444	35,698	37,552	39,231	41,748	43,746
Paper, Total	15,399	15,833	16,537	17,300	18,180	19,019
Newsprint	2,004	2,054	2,105	2,213	2,296	2,097
Groundwood paper, uncoated, total	938	907	910	956	952	1,029
Publication and printing	747	746	755	807	790	863
Converting paper	168	128	129	122	132	131
Miscellaneous groundwood	23	34	26	28	30	36
Paper, machine coated printing & converted paper, total	1,875	2,140	2,269	2,401	2,620	2,847
Coated, one side	138	267	281	297	321	340
Coated, two sides	1,737	1,873	1,988	2,104	2,399	2,517
Book Paper, uncoated, total	1,887	1,654	1,760	1,886	1,990	2,117
Publication and printing	1,052	1,037	1,061	1,152	1,219	1,316
Converting	816	608	680	731	767	800
Miscellaneous book paper	19	8	19	4	4	
Fine paper, total	1,776	1,924	2,054	2,104	2,210	2,410
Writing paper, total	1,371	1,487	1,569	1,600	1,700	1,875
Writing, rag (include index)	115	119	118	119	120	124
Writing, chemical wood pulp	1,256	1,368	1,451	1,481	1,580	1,751
Bristols, except rag index and bogus	126	134	149	156	155	147
Cover, text, and colored school paper	131	149	157	172	176	181
Thin paper	148	154	180	175	179	206
Coarse paper, total	3,957	3,997	4,124	4,251	4,396	4,588
Wrapping paper, total	566	544	583	576	601	615
Unbleached kraft	351	348	378	384	409	375
Other coarse	215	196	204	191	192	240
Shipping sack paper, total	880	891	867	952	962	980
Unbleached kraft	820	830	807	885	889	905
Rope and combination kraft and rope	60	61	60	67	73	75
Bag paper, total	1,257	1,266	1,339	1,382	1,481	1,606
Unbleached kraft	1,154	1,144	1,204	1,251	1,342	1,421
Other coarse	103	122	134	130	138	183
Converting paper, total	1,077	1,111	1,146	1,148	1,157	1,189
Unbleached kraft	636	637	655	665	673	679
Other converting	441	474	491	483	484	510
Glassine, greaseproof, and vegetable parchment, all end uses	177	184	191	194	196	199
Special industrial paper (including absorbent paper)	760	844	902	916	971	1,085

TABLE E-4. (Continued)

	1960	1961	1962	1963	1964	1965[(a)]
Sanitary tissue stock, total	1,964	2,077	2,179	2,340	2,518	2,622
Toweling	518	563	608	666	733	807
Napkin	238	247	249	263	269	290
Toilet tissue	878	936	985	1,055	1,109	1,113
Facial tissue stock other than napkin and toilet	278	262	262	279	326	321
Other sanitary tissue stock and sanitary napkin stock wadding	52	(b)	(b)	(b)	(b)	95
Tissue paper, except sanitary and thin paper	238	234	235	236	227	225
Paperboard, total	15,676	16,474	17,486	18,239	19,623	20,760
Containerboard, total	8,636	9,251	9,925	10,425	11,420	12,249
Liners	5,966	6,356	6,770	7,124	7,850	8,458
Corrugating material	2,443	2,664	2,866	3,022	3,239	3,494
Container chipboard	227	231	288	280	331	297
Folding boxboard, except special food board	2,940	2,878	3,050	3,166	3,325	3,292
Special food board	1,466	1,596	1,727	1,737	1,848	2,060
Setup boxboard	767	609	661	637	649	644
Special paperboard, total	1,867	2,140	2,123	2,276	2,381	2,514
Special paperboard	1,262	1,276	1,464	1,582	1,663	1,698
Other bending board	192	263	250	240	225	284
Other nonbending board	292	410	307	345	365	441
Cardboard	121	136	102	109	128	92
Wet Machine Board, total	175	155	146	141	148	135
Binder's board	53	54	58	55	59	(b)
Shoe board	57	59	61	58	58	46
Other wet machine board	65	42	26	30	31	(b)
Construction Paper and Board, Total	3,194	3,236	3,382	3,551	3,797	3,833
Construction paper	1,410	1,395	1,429	1,453	1,534	1,554
Hardboard and insulating board, total	1,784	1,845	1,953	2,098	2,263	2,279
Insulating board density 26 lb or less per cu ft:						
Short tons	1,098	1,084	1,080	1,139	1,215	1,268
Thousand square feet (1/2" basis)	2,848	2,850	2,885	3,039	3,266	3,457
Hardpressed wood fiber board, density over 26 lb per cu ft	686	762	873	959	1,048	1,010

(a) Preliminary.

(b) Withheld to avoid disclosing figures for individual companies.

Source: Bureau of the Census, Industry Division.

TABLE E-5. GEOGRAPHICAL DISTRIBUTION OF PULP AND PAPER PRODUCTION - 1964

Thousands of Short Tons

Division and State	Wood-Pulp Production	Paper and Paperboard Production: Total All Grades	Paper	Paperboard	Wet Mach. Board	Construction Paper and Board
United States, Total	32,429	41,748	18,180	19,623	148	3,797
Northeast	3,201	9,068	5,598	2,674	(a)	(a)
New England	2,002	3,802	2,890	715	(a)	(a)
Maine	1,726	1,959	1,897	(a)	(a)	(a)
New Hampshire	189	351	288	(a)	(a)	--
Vermont	(a)	(a)	48	296	--	--
Massachusetts	(a)	894	583	(a)	(a)	(a)
Rhode Island	(a)	(a)	--	(a)	--	--
Connecticut	(a)	418	74	312	(a)	(a)
Middle Atlantic	1,199	5,265	2,707	1,959	(a)	(a)
New York	537	1,974	1,377	579	(a)	(a)
New Jersey	70	1,306	261	750	(a)	271
Pennsylvania	592	1,986	(a)	630	(a)	(a)
North Central	3,331	9,028	4,150	3,856	(a)	(a)
East North Central	2,542	7,762	3,697	3,480	(a)	(a)
Ohio	309	1,801	715	969	--	117
Indiana	(a)	347	(a)	306	--	(a)
Illinois	(a)	832	(a)	480	(a)	266
Michigan	570	2,158	818	1,196	(a)	(a)
Wisconsin	1,407	2,624	2,080	528	--	(a)
West North Central	789	1,266	453	375	--	438
Nebraska	--	0.5	--	--	--	(a)
Minnesota	(a)	988	453	(a)	--	325
Iowa	(a)	108	--	(a)	--	(a)
Missouri	(a)	102	--	(a)	--	(a)
Kansas	--	67	--	(a)	--	(a)
South	19,711	18,012	6,174	10,292	(a)	(a)
South Atlantic	11,473	10,090	2,448	7,243	(a)	(a)
Delaware	--	66	(a)	(a)	--	--
Maryland	(a)	469	302	(a)	--	(a)
Virginia	(a)	1,630	345	1,214	(a)	(a)
West Virginia	--	35	(a)	(a)	--	--
North Carolina	1,541	1,332	505	786	--	(a)
South Carolina	1,722	1,564	266	1,270	--	(a)
Georgia	3,653	2,990	495	2,297	--	197
Florida	2,825	2,004	498	1,485	--	(a)
East South Central	3,938	3,654	1,882	1,064	(a)	(a)
Tennessee	904	1,093	(a)	444	(a)	(a)
Alabama	1,932	1,819	1,155	569	(a)	(a)
Mississippi	1,102	742	(a)	51	--	(a)
West South Central	4,300	4,268	1,844	1,984	--	440
Arkansas	(a)	982	565	(a)	--	(a)

TABLE E-5. (Continued)

			Paper and Paperboard Production			
Division and State	Wood-Pulp Production	Total All Grades	Paper	Paperboard	Wet Mach. Board	Construction Paper and Board
West South Central						
Louisiana	1,977	2,179	805	1,171	--	204
Oklahoma	(a)	193	--	(a)	--	(a)
Texas	905	914	474	326	--	113
West	6,186	5,639	2,258	2,802	--	579
Mountain	585	527	(a)	(a)	--	(a)
Idaho	(a)	190	(a)	(a)	--	--
Colorado	--	(a)	--	(a)	--	--
Montana	(a)	(a)	--	(a)	--	--
New Mexico	--	(a)	--	--	--	--
Arizona	(a)	(a)	(a)	(a)	--	--
Pacific[b]	5,601	5,112	(a)	(a)	--	(a)
Washington	3,797	2,195	1,351	(a)	--	(a)
Oregon	(a)	1,492	603	616	--	273
California	(a)	1,426	(a)	(a)	--	256

Source: Bureau of the Census, Industry Division.

(a) Withheld to avoid disclosing figures for individual companies.
(b) Includes data for Alaska and Hawaii.

Neutral Sulfite - Semichemical Pulping Process. Growth of this process is expected to bring United States output to 3 million tons in 1965 and to 5.2 million short tons in 1975. This process requires from 20 to 100 pounds of sulfur, depending on bleaching needs, for an average of 70 pounds per ton of pulp. In terms of soda ash, 250 to 460 pounds are required, again according to the bleaching requirements. There is evidence that caustic soda may be substituted for soda ash in this pulping operation.

The most rapidly growing and most important process for pulping is the kraft process, with a 1955 output of 11.6 million short tons and 32 million tons expected by 1975. In this process, sodium sulfide (introduced as sodium sulfate or less often as sodium sulfite) and caustic soda are used. The resulting black liquor containing saponified resin and fatty acids is skimmed and acidified, giving the kraft mill a by-product potential of crude tall oil - a source of rosin and fatty acids. Another important by-product of the kraft industry is sulfate turpentine.

Assuming that 60 percent of total United States pulp production in 1975 will be by the kraft process, a major portion of total United States salt-cake production will be required to produce the 32 million tons of kraft pulp projected for 1975.

Table E-6 shows the various chemicals used in pulp manufacture and estimated consumption in 1965. During the next decade, there should be a sharp rise in the use of caustic soda and salt cake, which are the key ingredients in the kraft process; less growth is foreseen in the amounts of soda ash used, and still less in the other chemicals for pulp manufacture.

Pulp Bleaching. Table E-7 shows the current consumption of some of the specialty bleaching chemicals. The growth pattern in pulp bleaching is indicated to be over 4 percent annually. The basic chemicals used are chlorine, lime, and caustic soda. Bleaching consists of the chlorination stage, with a subsequent calcium hypochlorite stage and caustic soda washing. There are variations in this process, depending on whether sulfite or kraft pulp is used. In the last 10 years, peroxide, and particularly chlorine dioxide, have become important for the final bleaching.

Sodium chlorate is growing as a source of chlorine dioxide in the bleaching field. This could have an important effect on the consumption of chlorine. The projected 14,000,000 tons of bleached kraft pulp in 1975 could possibly feel the impact of the Rapson sodium chlorate process. Table E-8 attempts to show what influence the Rapson process may have on chemicals for pulp bleaching. Announcements by Du Pont, Champion, and Weyerhaeuser that the addition of 2 to 6 percent of sulfamic acid to the normal chlorination-hypochlorite bleaching process improves paper strength may also influence sodium chlorate consumption.

Paper and Paperboard Manufacture. Table E-9 lists some of the major materials and estimates their consumption by the papermaker to impart such important paper properties as water resistance, grease resistance, opacity, internal fiber bond strength, dry strength, wet strength, absorbency, and the like.

The growth in clay reflects the continued growth rate in coated paper. As an internal additive for fillers and for opacity, its position is threatened by calcium carbonate - particularly in the neutral sheets where permanence and opacity are requisites. The

TABLE E-6. CHEMICALS USED FOR PULP MANUFACTURE IN 1965(a)

	Estimated Consumption, short tons
Salt Cake (Sodium Sulphate)	850,000
Lime	875,000
Limestone	260,000
Sulphur	560,000
Soda Ash	500,000
Caustic Soda	465,000
Sodium Sulphite	138,000
Ammonia	73,000
Sulphur Dioxide	35,000

(a) Forecast based upon the following references:

Chemical	Reference	Estimated Consumption
(1) Salt cake	1960 Chemical Engineering	925,000 tons
	Report at 90 lb/ton today	850,000 tons
(2) Lime	U.S. Bureau of Mines, 1960	838,000 tons
	1963	788,000 tons
(3) Limestone	Chemical Engineering, 1960	191,000 tons
(4) Sulfur	Chemical Engineering, 1960	477,000 tons
(5) Soda ash	Oil, Paint, and Drug Reporter, May 20, 1963	513,000 tons (1962)
	Chem. Eng. News, August 26, 1963	470,000 tons (1962)
	1960 Chemical Engineering Report	419,000 tons (1960)
(6) Caustic soda	Chemical Engineering 1960	332,000 tons
	Dow Chemical 1970 Est.	700,000 tons
(7) Sodium sulphite	Chemical Engineering, 1960	100,000 tons
(8) Ammonia	Chemical Engineering, 1960	62,000 tons
(9) Sulfur dioxide	Oil, Paint, and Drug Reporter, April 1, 1964 (48% of total to paper)	

TABLE E-7. CHEMICALS USED FOR PULP BLEACHING IN 1965[a]

	Estimated Consumption, short tons
Chlorine	940,000
Sodium Chlorate	85,000
Hydrogen Peroxide	6,300
Sodium Peroxide	6,300
Sodium Hypochlorite	116,000
Zinc Hydrosulphite	5,300

(a) Forecast based upon the following references:

Chemical	Reference	Estimated Consumption
(1) Chlorine	Chem. Week, January 2, 1965 5.4 billion tons total	16.5% to paper
(2) Sodium chlorate	Oil, Paint, and Drug Reporter, January 21, 1965	70,000 tons (1962)
	Chemical Engineering Report	37,000 tons (1960)
(3) Hydrogen peroxide	Oil, Paint, and Drug Reporter, April 1, 1964	11,700,000 lb
(4) Sodium peroxide	Chemical Engineering, 1960	5,000 tons
(5) Sodium hypochlorite	Chemical Engineering, 1960	90,000 tons
(6) Zinc hydrosulfite	Chemical Engineering, 1960	4,500 tons

TABLE E-8. POSSIBLE IMPACT OF NEW BLEACHING PROCESS ON BLEACHING CHEMICALS

1965 BL Kraft 8,200,000 Tons Estimated
1975 BL Kraft 14,000,000 Tons Projected

	Tons in 1964	Total Tons in 1975	
		No Technical Change	Rapid Changeover to Rapson Process[a]
Chlorine	891,000	1,490,000	440,000
Sodium Chlorate	80,000	133,000	(700,000)
Hydrogen Peroxide	6,000	10,000	10,000
Sodium Peroxide	6,000	10,000	10,000
Sodium Hypochlorite	110,000	150,000	150,000
Zinc Hydrosulphite	5,000	7,500	7,500
Other Pulping Chemicals Affected			
Caustic Soda	430,000	755,000	135,000
Salt Cake	800,000	1,350,000	720,000

(a) An unlikely development -- total conversion.

TABLE E-9. CHEMICALS USED IN PAPER AND PAPERBOARD MANUFACTURE

Estimated Consumption in Short Tons

	1960	1965	1970
Corn Starch (excluding converting)	385,000	450,000	550,000
Alum (excluding water treatment)	355,000	375,000	460,000
Rosin Sizing (70% basis)	194,000	210,000	265,000
Defoamers	17,000	20,500	24,500
Titanium Dioxide	71,000	130,000	206,000
Calcium Carbonate	24,000	150,000	200,000
Wax Sizing (excluding building products)	30,000	33,000	37,000
Latexes	11,000[a]	30,500	38,000
Wet-Strength Resins	19,000	24,000	37,000
Casein	9,300	23,000	26,000
Clay	938,000	1,680,000	2,000,000

(a) Excludes coating adhesives.

growth rate in alum is dependent largely upon the requirements for internal addition with rosin size to produce aluminum resinate for water resistance. Sodium aluminate is used at times in conjunction with alum. Corn starch competes with other types of starches as a strength additive and as a surface treatment agent in fine papers. Sodium resinate (rosin sizing) is the basic chemical agent for developing resistance to aqueous penetration in the sheet of paper. Sizing agents also are available that do not require the use of alum, thereby permitting the manufacturer to produce a neutral or alkaline sheet. Wax and wax emulsions impart specific water resistance and are used to develop finish. Prior to the advent of polyethylene film, paraffin wax was used as the coating material in milk cartons. Through the inclusion of modifying resins such as polyvinylidenes, it may regain some of this market. Titanium dioxide is an important pigment material, both in coatings and in internal application for opacity and brightness. The growth in titanium dioxide, expected to reach 185,000 short tons by 1968, shows that in the recent 5-year period, the ratio of pigment to paper has doubled. Wet-strength additives fulfill the need for disposable household papers, frozen foods, and milk-container boards. The wet-strength resins are primarily urea formaldehyde and melamine formaldehyde. More recently, polyamide epichlorohydrin resin has become important for developing wet strength in a neutral or alkaline sheet. Also, polyethyleneimine imparts wet strength to paper without the necessity of curing. Surface sizing of paper handsheets using dispersions of dialdehyde starch prepared with sodium bisulfite or borax provides excellent improvement in dry-strength properties in addition to high wet strength. The growth rate in urea formaldehyde and melamine-formaldehyde resins is about 6 percent per year. This approximates the average of 5.5 percent growth in wet-strength grade of papers.

Other chemicals used in paper and paperboard manufacture are defoamers, casein (to help impart crimp), optical whitening agents, dyes, and retention aids. The market for retention aids has developed rapidly in the last 5 years as the result of higher machine speeds, higher cost fillers, the need to upgrade paper from the standpoint of opacity and lower basis weight, and elimination of stream pollution. Retention aids include a broad range of polyelectrolytes such as proteins, natural gums, cationic starches, quaternized polyethyleneimine, and acrylic acid ester-vinyl-type cationic polymers.

Recent Research

- A new Canadian process converts all the oxidizing equivalents in sodium chlorate to available chlorine, consumes all the sulfuric acid fed, and produces salt-cake by-product. All the products are usable in a bleached kraft pulp mill, resulting in substantial cost savings, and elimination of waste-disposal problems.

- The addition of a small amount of sulfamic acid to normal bleaching chemicals in pulp manufacture improves paper strength.

- A dry papermaking process that may halve the cost of a paper mill is undergoing pilot-plant tests in Denmark.

- Canadian research on the chlorination process showed that any pulp – kraft or sulfite – required a contact period of no more than 60 seconds at consistencies of 20 to 30 percent.

- Recent tests showed that a small percentage of wax can replace a big percentage of rosin in sizing.
- Partial replacement of titanium dioxide by sodium silico-aluminate yields papers having the same opacity but with a gain in brightness.
- New-type pulping systems aimed at moderating or elimination pollution problems continue to be subjects of investigation.
- Epidemic nosebleeds were found to follow chemical changes in the fabrication of two brands of blue-dyed apple-packing trays made from salvaged newspapers.
- Methods based on chemical modification of groundwood pulp are accompanied by greater brightness and greater stability of pulp.
- A peracetic-acid-treated mechanical pulp was found to be superior to the same pulp when treated with sodium chlorite or when cooked by a neutral sulfite process.
- The market for fluorochemical paper sizes could expand greatly if the Food and Drug Admisistration approves their use in contact with human or pet foods.
- Three new polymeric starch dialdehydes were introduced for the 500-million-lb/yr market for adhesives in paper coatings.

Toxicity Information

Gefafer, in a review of the occupational hazards found in the paper making, paper treating, and paper dyeing industries, lists the following chemicals as potentially dangerous:(E-13)

Acrylonitrile
Alkalies
Aluminum and compounds
Amino resins
Ammonia
Arsenic compounds
Barium salts
Calcium oxide
Calcium bisulfite
Chloride of lime
Chlorinated diphenyls
Chromium compounds
Formaldehyde
Formic acid
Glues
Hydrogen sulfide
Mercury
Oxalic acid
Potassium lye
Resins
Rosins
Sodium hydroxide
Sodium sulfate
Sodium sulfide
Sulfur dioxide
Sulfur trioxide
Sulfuric acid
Selenium and compounds
Talc
Tin and compounds
Titanium and compounds
Zinc and compounds.

This list continues to be supplemented with new chemicals for pulp and paper processing. It can probably be assumed that employee exposure to these and new potentially toxic agents is well controlled by present-day industrial hygiene practices. However, we need to be aware of the use, quantity, and disposition of the agents to determine whether they are finding their way to our environment to produce an environmental hazard. For example, nosebleed of apple packers was attributed to dyes present in salvaged newspaper used in the manufacture of packing trays. Nosebleeds stopped when the workers switched to plastic trays.

Toxicology

A preceding section considered the amounts and kinds of wastes that are being created by the industry. The more important materials found in those wastes are presented in Table E-10, which shows the toxicity of the agents as found in reference tests. The first five agents - hydrogen sulfide, methyl disulfide, methyl mercaptan, methyl sulfide and sulfur dioxide - compose the more important volatile waste products. Several of these agents and many of the others are considered highly toxic and therefore should be evaluated for their potential contribution to health hazards.

In Table E-10 are shown the allowable concentrations (threshold limits) and a general evaluation ("toxicity") of the agent's toxicity. Toxicity ratings in the table are those of Sax (E-14) as expressed when known for acute local, acute systemic, chronic local, and chronic systemic poisoning. "Slight" indicates reversible changes that disappear after exposure ends; "moderate" indicates irreversible and reversible changes, not severe enough to cause death or permanent injury; and "high" indicates death or permanent injury after very short exposure to small quantities. The maximum toxicity reported is shown.

Presumably, little or none of this toxicological information is based on clinical data and should be so viewed to avoid potentially misleading conclusions. Epidemiological data and environmental pollution contributions by the industry are not readily available from the literature.

If quantitative data should indicate that the polynuclear aromatic compounds are emitted into the atmosphere in carcinogenic concentrations, a serious environmental hazard might result. This problem requires additional research before the seriousness of the situation can be determined.

Chemical Contaminants Resulting From Pulp and Paper Manufacture

An examination of the pulp and paper processes indicates the formation of many products that might serve as environmental hazards in the air, water, soil, or in contact with man. A review of this problem was not readily available in the literature.

Pulp Processing. Blowpit gases from the sulfite digester during pulping contain principally steam, air, sulfur dioxide, and small amounts of methanol, ethanol, terpenes, cymenes, and organic sulfur compounds. If the gases are allowed to escape into the

TABLE E-10. TOXICITY OF MAJOR CHEMICAL AGENTS FROM THE PULP AND PAPER INDUSTRY

Agent	Threshold Limit[(a)], mg/m^3	Toxicity[(b)]
Hydrogen sulfide	28	High
Dimethyl disulfide		(c)
Methyl mercaptan	100	Moderate
Methyl sulfide	--	Probably high
Sulfur dioxide	13	Moderate (irritating)
Acetone	2400	Moderate
Camphene		Unknown
Chlorine dioxide	0.3	High
Ethyl alcohol	1880	Moderate
Isobutyl methyl ketone	409	Moderate
Limonene		(c)
Methyl alcohol	262	Moderate (irritant)
α-Pinene		Moderate
β-Pinene		(c)
α-Terpineol		(c)

(a) Threshold limits suggested by the American Congress of Government Industrial Hygienists (E-14).

(b) Ratings as described by Sax (E-14)

(c) Information not available from References (E-13), (E-14), or (E-16).

atmosphere, there is a loss of about 25,000 pounds of steam and 2,000 pounds of sulfur dioxide for each 20-ton digester blown. Some mills have made installations to recover a large part of the heat and sulfur in the gases from the blowpit. The solids in spent sulfite liquor are composed of sugars, incompletely hydrolyzed carbohydrates, lignosulfonic acids, calcium sulfate, calcium bisulfate, and minor inorganic ingredients such as magnesium, sodium, and ammonium salts. Although some companies recover magnesium, sodium, and ammonium salts, most sulfite pulp mills do not utilize the spent liquor but dispose of it directly into streams, ocean waters, or lagoons. This is a highly undersirable situation from the standpoint of both economic waste and stream pollution.

The gases and black liquor from alkaline pulping contain many other chemicals besides the tall oil fraction. Especially deleterious are malodorous materials such as hydrogen sulfide, methyl mercaptan, dimethyl sulfide, and dimethyl disulfide. The principal source of these gases is from the digester relief and blow-down gases, but they also come from the washers, weak black liquor spillage, run off to sewer, turpentine recovery, evaporator condensate, smelters, lime kiln, or spent liquor sent to lagoons or streams. The mercaptan content of digester blow gases runs as high as several thousand pounds per day. The vapors from the relief of sulfate digesters also contain methanol and turpentine contaminated with the malodorous materials mentioned above, that are removable in part by fractional distillation. In some cases, the relief and blow gases are condensed and either burned or treated with an oxidant. An extension of this concept is black liquor oxidation to deactivate the malodorous compound.

Sulfur-containing solids formed during sulfate pulping are thiolignins and sulfate lignins. Mild acid treatment of the black liquor releases about 50 percent of the sodium lignates which can then be separated and converted into lignin by stronger acid treatment. Although many uses have been suggested and explored for lignin, (e.g., asphalt emulsions, compound agents in vinyl plastics, soil conditioner, oil well drilling-mud additive, insecticide dispersant, foundry sand binder, and absorber in lead-acid storage batteries), large scale applications are lacking.

In addition to the lignins, sulfate black liquor usually contains the tall-oil fraction, alkali, sodium sulfide, iron oxide, alumina, and small amounts of some other inorganic materials. The black liquor that is not recycled to the digesters is sent to the alkali recovery plant where a mixture of sodium hydroxide and sodium sulfide is recovered. In the average mill, about 90 to 95 percent of the total sodium and about half of the total sulfur are recovered for reuse. Much of the remaining sulfur is lost as hydrogen sulfide and sulfur dioxide. Calcium carbonate formed as a by-product in causticizing is burned in a kiln to form hydrated lime which is used in the causticizing step.

A study of emissions from digester relief and blow gas systems in the sulfate (kraft) pulp mill has been reported. The pulp mill located in Lewiston, Idaho, produces 450 tons per day of bleached paperboard and an additional 200 tons per day of market pulp by the kraft process. Based on practiced operating conditions, pollutants per ton of pulp produced were as follows:

Hydrogen sulfide	0.66 lb
Methyl mercaptan	5.3 lb
Dimethyl sulfide	3.8 lb

Chlorination of the digester gases and condensate is reported to be effective in reducing odorous emissions. If an efficiency of 98 percent is assumed, the sulfur compounds emitted are:

Hydrogen sulfide	8.6 lb/day
Methyl mercaptan	69.0 lb/day
Dimethyl sulfide	50.0 lb/day.

Table E-11 contains the overall picture on the atmospheric emissions from the kraft pulp mill. High concentrations of hydrogen sulfide and sulfur dioxide result from the recovery furnaces. Plant boilers and lime kilns contribute heavily to the oxides of nitrogen and hydrocarbons. The high hydrocarbon content probably results from the burning of wood.

The identification of nonsulfur organic compounds condensed out or adsorbed on salt-cake particles from the electrostatic precipitator following a recovery furnace, has been reported. Extraction followed by chromatography of the extract gave products whose ultraviolet absorption spectra corresponded to the polynuclear aromatic hydrocarbons benz [a] anthracene, benzo [a] pyrene, benzo [e] pyrene benzo [g, h, r] perylene, chrysene, coronene, fluoranthene, and pyrene. Benzo [a] pyrene is commonly referred to as a strong carcinogen; the other hydrocarbons may be weakly carcinogenic. The results reported are qualitative, and no attempt was made to obtain quantitative data.

Bleaching. An examination of Table E-7 suggests that several contaminants might be generated in the use of the listed chemicals. Chlorine itself could become a contaminant if used unwisely. The bleaching action of sodium chlorate is attributed to the formation of chlorine dioxide and chlorine, both of which could serve as contaminants. This could become especially significant if the predicted increase of sodium chlorate materializes (Table III). The possible deleterious effects of sulfur dioxide obtained in bleaching with zinc hydrosulfite also must be recognized.

Paper and Paperboard Manufacture. Although at present there may not be contamination alarms about the major chemicals listed in Table E-9, the identification in the text of the report of other chemicals used in paper and paperboard manufacture may be cause for concern. For example, the use of fluorescent brighteners, dyes, retention aids, and grease and waterproofing agents could conceivably lead to environmental hazards. In this respect, a new disease of apple packers appeared in 1964 in the State of Washington. Blood in nasal discharges ranged from mild staining to dripping hemorrhage. The disease followed chemical changes in the fabrication of two brands of blue-dyed apple-packing trays made form slavaged newspaper. A third tray made of plastic and a fourth of virgin wood pulp produced no such signs of nasal irritation. Nosebleeds decreased when useage of newsprint trays was stopped. (JAMA, 1966)(E-15)

TABLE E-11. SUMMARY OF ESTIMATED EMISSIONS FROM KRAFT PULP MILL

Process or Equipment Source	Emissions, lb/day										
	Hydrogen Sulfide	Methyl Mercaptan	Dimethyl Sulfide	Solid Particulates	Combustibles[(a)]	Sulfur Oxides as SO_2	Nitrogen Oxides as NO_2	Aldehydes as Formaldehydes	Organic Acids as Acetic Acid	Hydrocarbons	Water Vapor
Digester gases	9	69	50	--	--	--	--	--	--	--	--
Evaporators	390	20	Negligible	--	--	--	--	--	--	--	--
Recovery furnaces	3,120	Negligible	Negligible	12,310	141,400	1,180	(c)	--	--	--	2,778,000
Smelt tanks	(c)	(c)	(c)	1,100	--	--	--	--	--	--	--
Lime kilns	737	(c)	(c)	6,269	147,700	6[(b)]	847	8	20	--	1,850,000
Oxidation towers	(c)	(c)	60	--	--	--	--	--	--	--	--
Plant boilers[(d)]	--	--	--	397	Negligible	28[(b)]	2,910	141	92	1,285	2,550,000
Paper machines	--	--	--	--	--	--	--	--	--	--	1,782,000
Pulp dryer	--	--	--	--	--	--	--	--	--	--	320,000
Total	4,256	89	110	20,076	289,100	1,214	3,757	149	112	1,285	9,280,000

(a) Combustible emission probably consists of carbon monoxide and other organic materials.

(b) Assumed sulfur content of natural gas, 0.4 grain/100 ft^3.

(c) Present in emissions, but in unknown amounts.

(d) Emissions include those from burning waste wood.

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*Although not needed for obtaining the information contained in this report, the following additional references should be made available to maintain a technological overview of the pulp and paper industries:

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